Poly(pyridine-2,5-diyl)–$CuCl_2$ catalyst for synthesis of dimethyl carbonate by oxidative carbonylation of methanol: catalytic activity and corrosion influence

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A π-conjugated polymer, poly(pyridine-2,5-diyl) (PPy) was investigated as a support for $CuCl_2$ in the synthesis of dimethyl carbonate by oxidative carbonylation of methanol. The PPy–$CuCl_2$ adduct had high catalytic activity which was comparable to that of the homogeneous $CuCl_2$ catalyst. The adduct caused corrosion of stainless-steel vessels only to minor extent, compared with the homogeneous $CuCl_2$ catalyst. This PPy–$CuCl_2$ catalyst was easily recycled by filtration and showed a similar catalytic activity in the third time use. The presence of the π-conjugated system in PPy, through which electrons can move, may bring about the high catalytic activity for the oxidative carbonylation of methanol, which involves Cu(II)/Cu(I) redox processes.

Keywords: dimethyl carbonate (DMC), oxidative carbonylation, $CuCl_2$ immobilization, corrosion resistance

1. Introduction

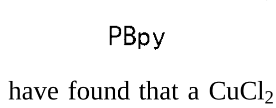
Dimethyl carbonate (DMC) has been given much attention as a replacement for toxic phosgene and dimethyl sulfate, and various routes to synthesize DMC have been found. Among them, the oxidative carbonylation of methanol (equation (1)) over a copper chloride catalyst is especially effective and industrially adopted. However, deactivation of the catalyst by ligand exchange with OH^- and by oxidation with O_2 is unavoidable during the reaction. It requires a catalyst regeneration procedure by adding HCl into the reactor [1].

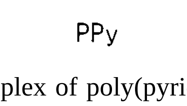
$$CO + 2CH_3OH + (1/2)O_2 \rightarrow (CH_3O)_2CO + H_2O \quad (1)$$

The existence of Cl^- in aqueous media, under the condition of the redox of Cu, is considered to induce severe corrosion to metallic materials [2]. The industrial process uses a slurry liquid-phase system, and efforts have been made to suppress a high corroding effect of Cl^- toward the equipment made of metals.

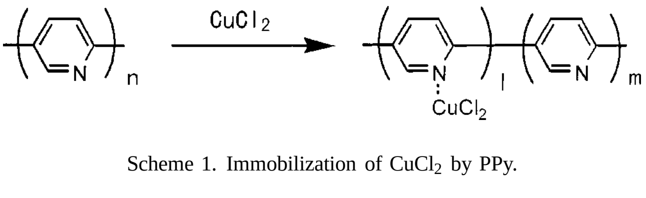
Supported copper chloride catalysts are less corrosive, and have been used for the DMC synthesis, especially in vapor-phase systems [3,4]. High catalytic activities were attained by choosing activated carbon as a support [5]. On the other hand, polymers containing pyridine units as a coordinating group for $CuCl_2$ were found to be effective supports for the DMC synthesis in liquid phase. The severe corrosion effect was appreciably suppressed. For example, poly(vinylpyridine) [6] has been reported to be a good support for $CuCl_2$. However, the high catalytic activity of $CuCl_2$ is considerably decreased by the complex formation with poly(vinylpyridine).

Several π-conjugated polymers are known to be effective as supports, particularly, for Pd and Cu in Wacker-type reactions, to promote the redox of coordinated metals through the π-conjugated spacer [7–10]. Recently, we prepared a novel type of polymer-supported $CuCl_2$ catalysts [12–14] for the DMC synthesis. Among them, a $CuCl_2$ complex of π-conjugated poly(2,2′-bipyridine-5,5′-diyl) (PBpy) [11] had higher catalytic activity and stability than the poly(vinylpyridine)–$CuCl_2$ catalyst [14]. The presence of the π-conjugated system in the polymer is considered to facilitate the redox reaction of copper involved in the catalytic reaction [14,15].


PBpy


PPy

We have found that a $CuCl_2$ complex of poly(pyridine-2,5-diyl), PPy (scheme 1) [11], which has a similar π-conjugated system, also shows high catalytic activity in the



Scheme 1. Immobilization of $CuCl_2$ by PPy.

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DMC synthesis. Herein we report the preparation of the PPy–$CuCl_2$ complex, its catalytic activity, and its corrosive effect to stainless steels. Revealing of usefulness of such π-conjugated polymers as supports of metal catalysts will be important for developing new catalytic systems.

2. Experimental

PPy was synthesized as follows. 2,5-dibromopyridine (400 g, 1.69 mol) purchased from Tokyo Kasei Co., Ltd. was polymerized by using $Ni(PPh_3)_4$ as a debrominating reagent [11]. $Ni(PPh_3)_4$ was prepared *in situ* from $NiCl_2$ (263 g, 2.03 mol), Zn powder (133 g, 2.03 mol), and triphenylphosphine (PPh_3) (2130 g, 8.11 mol) in DMF (8.40 l). After several times of washing in a manner described in [11], PPy was obtained as an orange-yellow powder (117 g, 90% yield). It was reprecipitated from a $HCOOH/NH_3$ aqueous solution and dried under vacuum before the preparation of the PPy–$CuCl_2$ complex described below.

Inherent viscosity (η) of the obtained PPy was 0.27 $dl\,g^{-1}$ in HCOOH, which indicated that the polymer had a molecular weight of about 2000 or lower, as judged from the η value of 0.85 $dl\,g^{-1}$ obtained for PPy with a molecular weight of 3800 [11]. It was reported that use of $Ni(PPh_3)_4$ gave PPy with a molecular weight of 1600 [11].

The PPy powder and the 2 equivalent of $CuCl_2$ in methanol were allowed to react for 5 h under reflux, and the PPy–$CuCl_2$ catalyst was obtained as a greenish-yellow powder which was not soluble in methanol. A part of $CuCl_2$ will take a chelating coordination mode of a head-to-head unit (2,2′-bipyridine-like unit) of the polymer [11]. X-ray fluorescence spectrometry (XRF) revealed that the obtained complex contained 18.7 wt% of Cu and 18.9 wt% of Cl. After the first use in the catalytic reaction, 15.5 wt% of Cu and 15.4 wt% of Cl were found, and after the three times recycled use, 13.9 wt% of Cu and 13.8 wt% of Cl were found.

The DMC synthesis was performed according to the following procedure. In an autoclave, 10 ml (7.75 g) of methanol, which served as the substrate and solvent, and PPy–$CuCl_2$ powder (719 mg) were added ([Cu] $=$ 150 mM). Then, CO (23 $kgf\,cm^{-2}$), and O_2 (2 $kgf\,cm^{-2}$) were introduced in the autoclave. After the reaction at 140 °C for 2 h, concentrations of DMC, methanol, CO_2, and O_2 were analyzed by gas chromatography. CH_3OH conversion (%) ($=$produced DMC$/$(introduced $CH_3OH/2$)), DMC yield (%) ($=$produced DMC$/$(introduced $O_2 \times 2$)), and DMC selectivity (%) ($=$DMC$/$(DMC $+$ CO_2)) were calculated from the gas chromatographic data.

The rate of corrosion (in $mg\,h^{-1}$) during the reaction was measured separately. The test pieces (about 15 mm × 6 mm × 2 mm) of SUS316 (Cr 18%, Mo 2%, Ni 10%, C 0.08%, Fe base, weight $= 2.0 \pm 0.2$ g) and Hastelloy C(HC)276 (Cr 16%, Mo 16%, Fe 5%, C 0.01%, Ni base, made by Mitsubishi Material, weight $= 3.0 \pm 0.3$ g) were introduced into the reactor. Reaction time was 2 h for each run. The weight loss of the test pieces was measured after the first and third catalytic reactions.

3. Results and discussion

The catalytic activity (DMC yield and DMC selectivity) of the PPy–$CuCl_2$ catalyst (e.g., PPy–$CuCl_2$ (1st use) in table 1) was compared with those of the homogeneous $CuCl_2$ catalyst and the PBpy–$CuCl_2$ catalyst at a CH_3OH conversion of about 3%, and the results are shown in table 1. Under the reaction conditions, no by-product other than CO_2 was detected by gas chromatography, and the DMC selectivity was calculated from the following equation: DMC/(DMC $+$ CO_2).

Recently, we reported that PBpy gave higher catalytic activity in the $CuCl_2$-promoted DMC synthesis than poly(vinylpyridine), which is one of the most generally used supports for $CuCl_2$ (cf. the last line in table 1) [14]. A reaction mechanism involving Cu(II)/Cu(I) redox processes has been proposed for the DMC synthesis using the copper chloride catalyst [16]:

$$2CuCl_2 + 2CH_3OH \rightarrow 2CuCl(OCH_3) + 2HCl \qquad (2)$$

$$2CuCl(OCH_3) + CO \rightarrow 2CuCl + DMC \qquad (3)$$

$$2CuCl + (1/2)O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O \qquad (4)$$

The presence of the π-conjugated system in PBpy was suggested to make occurrence of the Cu(II)/Cu(I) redox processes easier by providing electrons or holes through the π-conjugated system [14].

The molar ratio of Cu per the pyridine unit was 40 mol% before the catalytic reaction (just after the preparation) in the PPy–$CuCl_2$ catalyst. The amount of Cl_2 per the pyridine unit was 34 mol% (or 68 mol% of Cl) which is lower than that of Cu, indicating that all of the coordinated Cu species did not exist as $CuCl_2$. Similar results were reported for the activated carbon-supported $CuCl_2$ catalyst [17], and it

Table 1
Catalytic activity of the PPy–$CuCl_2$ catalyst in comparison with those of the PBpy–$CuCl_2$ catalyst, the poly(vinylpyridine)–$CuCl_2$ catalyst, and the homogeneous $CuCl_2$ catalyst.[a]

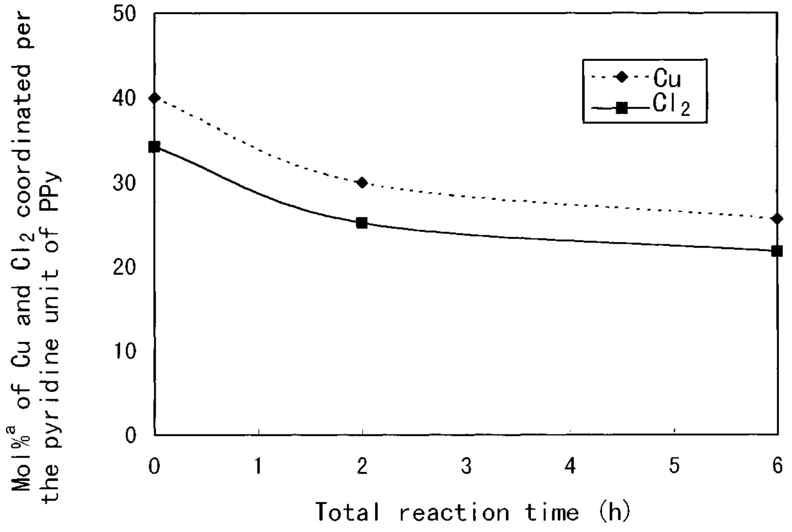
Catalyst[b]	CH_3OH conv.[c] (%)	DMC yield[c] (%)	DMC sel.[c] (%)
PPy–$CuCl_2$ (1st use)	2.96	71.3	94.4
PPy–$CuCl_2$ (2nd use)	2.69	65.0	93.3
PPy–$CuCl_2$ (3rd use)	2.71	66.4	93.9
PBpy–$CuCl_2$[d]	2.72	68.1	94.2
Homogeneous $CuCl_2$[d]	2.76	70.0	97.4
Poly(vinylpyridine)–$CuCl_2$[d]	1.84	47.1	91.4

[a] [Cu] $=$ 150 mM, CH_3OH $=$ 10 ml, CO $=$ 23 $kgf\,cm^{-2}$, O_2 $=$ 2 $kgf\,cm^{-2}$, temp. $=$ 140 °C, reaction time $=$ 2 h.

[b] In the 2nd and 3rd uses, freshly prepared catalyst was added to adjust [Cu] $=$ 150 mM.

[c] CH_3OH conv. $=$ produced DMC$/$(introduced $CH_3OH/2$), DMC yield $=$ produced DMC$/$(introduced $O_2 \times 2$), DMC sel. $=$ DMC$/$(DMC$+$$CO_2$).

[d] Reported in [14].



[a] Mol% is calculated from Cu, Cl contents in the PPy–$CuCl_2$ catalyst.

Figure 1. Leaching of $CuCl_2$ (Cu and Cl_2) from PPy.

was suggested that $CuCl_2$ was partly reduced to CuCl or received ligand replacement reactions (e.g., that to form CuCl(OH) by a reaction with H_2O).

As shown in table 1, the DMC yield and DMC selectivity of the PPy–$CuCl_2$ catalyst were comparable to those of the PBpy–$CuCl_2$ catalyst and the homogeneous $CuCl_2$ catalyst. The high yield and selectivity are also ascribed to the presence of the π-conjugated system in PPy. The PPy–$CuCl_2$ catalyst could be recycled, and high yield and selectivity were found in the third use (cf. the data of PPy–$CuCl_2$ (2nd use) and PPy–$CuCl_2$ (3rd use) in table 1), although the initial catalytic activity was somewhat decreased.

Some $CuCl_2$ leaching from the PPy support was observed during the catalytic reaction, and an argument that the released $CuCl_2$ exhibited some catalytic activity, is existing. The $CuCl_2$ leaching was also observed for the poly(vinylpyridine)–$CuCl_2$ catalyst [14], however, the catalyst apparently exhibited a lower activity than the PPy–$CuCl_2$ catalyst (table 1). Thus, the contribution of the released $CuCl_2$ to the DMC yield and selectivity is considered to be of insignificant level for comparing the data in table 1.

The amount of coordinated $CuCl_2$ was estimated before the reaction (0 h), after the first reaction (2 h), and after the third reaction (total reaction time = 6 h). The results are shown in figure 1, where mol% values of $CuCl_2$ (Cu and Cl_2) supported by the pyridine unit of PPy are plotted versus the total reaction time.

During the first catalytic reaction (0–2 h), the amounts of Cu and Cl_2 per the pyridine unit were decreased to 30 and 25 mol%, respectively. During the second and third catalytic reactions (2–6 h), the amounts of Cu and Cl_2 were eventually decreased to 26 and 22 mol%, respectively. PBpy has higher coordinating ability to Cu due to its having chelating units, and it was reported that only a negligible amount of Cu was lost from the PBpy support (18% of the initially supported Cl^- was lost after 6 h) [14].

Table 2
Rate of corrosion[a] caused by the PPy–$CuCl_2$ catalyst in comparison with the homogeneous $CuCl_2$ catalyst.

Catalyst	Rate of corrosion ($mg\,h^{-1}$)	
	SUS316[b]	HC276[b]
PPy–$CuCl_2$ (1st use)	0.5	0.3
PPy–$CuCl_2$ recycled (3rd use)	0.3	<0.1[c]
Homogeneous $CuCl_2$[d]	39.6	8.3

[a] Weight loss ($mg\,h^{-1}$) of test piece during the catalytic reaction.

[b] SUS316 (stainless steel): standard No. 316 (AISI), HC276 (stainless steel): standard No. B575 (ASTM).

[c] Within the limit of detection.

[d] Reported in [14].

Leaching of Cl^- to a larger extent was also observed during the initial step of the catalytic reaction using the activated carbon-supported $CuCl_2$ catalyst [5], and it was suggested that the ligand exchange of Cl^- with OH^- partly took place. The X-ray photoelectron spectroscopy study has been made for the poly(4-methyl-4′-vinyl-2,2′-bipyridine)-supported $CuCl_2$ catalyst [12]. It was confirmed that some reduction of Cu(II) took place at the catalyst preparation, and the reduction proceeded during the catalytic reaction with $CuCl_2$ leaching. However, these reduced chemical species have not been identified. We are trying to identify the reduced Cu element from the Auger electron spectroscopy measurement.

The rate of corrosion (in $mg\,h^{-1}$, cf. section 2) due to Cl^- was determined for the PPy–$CuCl_2$ catalyst, and the data are given in table 2. The data for the homogeneous $CuCl_2$ catalyst are also listed as the reference. The corroding influence to stainless steels was dramatically improved by the immobilization of $CuCl_2$ by the PPy support. However, pitting corrosion was still observed on the metal surface, similar to cases of the PBpy–$CuCl_2$ and poly(vinylpyridine)–$CuCl_2$ catalysts [14]. The corroding effect at the first catalytic use was larger than that at the recycled (third) use. This is consistent with the data shown in figure 1, which reveals that the Cl^- leaching takes place to a larger extent at the first use.

As described above, PPy seems useful as a support for $CuCl_2$ in the DMC synthesis. However, further improvement of the catalytic system is required. For example, prevention of the $CuCl_2$ leaching necessitates finding out of better reaction conditions (temperature, pressure, etc.). Modification of the PPy synthetic method may give PPy with stronger binding force toward $CuCl_2$. Elaboration of the procedure for making the PPy–$CuCl_2$ complex will also be important.

4. Conclusion

The new heterogeneous π-conjugated PPy–$CuCl_2$ catalyst showed high catalytic activity for the DMC synthesis from methanol, CO, and O_2. The catalyst was able to be recycled at least three times, keeping its initial catalytic activity. The catalytic activity was much higher than that of the poly(vinylpyridine)–$CuCl_2$ catalyst. The PPy–$CuCl_2$ catalyst showed excellent corrosion resistance toward stainless steels, compared with the homogeneous $CuCl_2$ catalyst.

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