



Novel Type of Heterogenized CuCl₂ Catalyst for Dimethyl Carbonate Synthesis

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博士論文

**Novel Type of Heterogenized CuCl₂ Catalyst
for
Dimethyl Carbonate Synthesis**

平成 13 年 1 月

神戸大学大学院自然科学研究科

佐 藤 靖

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**Novel Type of Heterogenized CuCl_2 Catalyst
for
Dimethyl Carbonate Synthesis**

ジメチルカーボネート合成用

銅系新規固相触媒の開発

平成 13 年 1 月

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Chapter 1

Backgrounds and Purposes of This Research

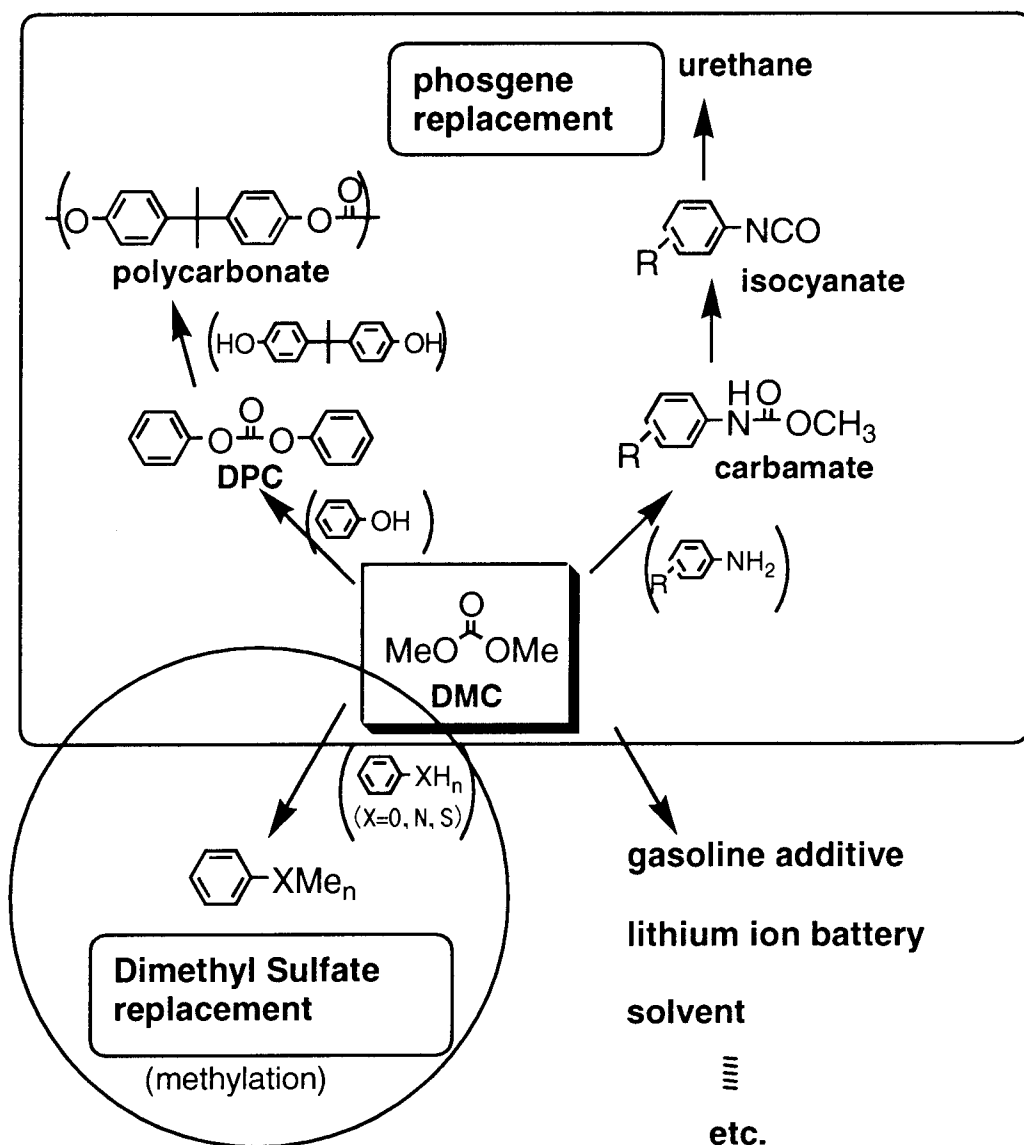
1. Dimethyl Carbonate Synthesis by Oxidative Carbonylation of Methanol

DMC is a useful compound as a methylating reagent to replace dimethyl sulfate and as reagents for carbonylation and methoxycarbonylation to replace phosgene and also as a solvent in organic synthesis and electrolyte in lithium-ion batteries. DMC is also useful as a gasoline additive due to its high oxygen content, good blending properties, low toxicity, and rapid biodegradability. In addition, it has been expected to be a safer substitute for toxic phosgene in polycarbonate synthesis and isocyanate synthesis (Scheme 1). Therefore, people paid much attention to DMC as a promising chemical compound in view of the increasing world wide environmental problem.

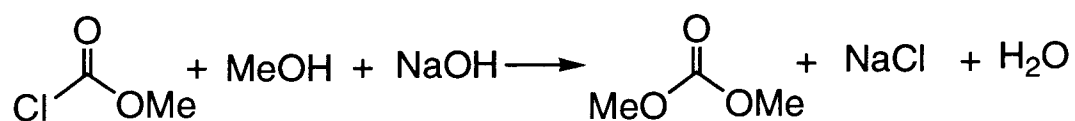
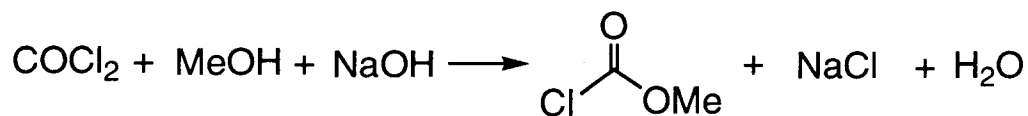
DMC was previously produced from phosgene. However, this route is not advantageous from the viewpoint of safety of handling highly toxic phosgene and the environmental problem of disposing of sodium chloride (Scheme 2).

Thus, other “non-phosgene” synthetic processes have been required. An “ethylene carbonate and methanol transesterification route to DMC” is one of the “non-phosgene” processes under progress (Scheme 3) [1]. Ethylene oxide and carbon dioxide are reacted to form ethylene carbonate. DMC is formed by the transesterification reaction between ethylene carbonate and methanol, with ethylene glycol as a coproduct. Thus, the overall process converts ethylene oxide to DMC with coproduction of ethylene glycol. Such technology would be of use only in coexistence with a glycol plant. This presents an unavoidable problem, namely that the equilibrium between ethylene carbonate and DMC lies so far to the former side, demanding a reactor of larger scale than usual. Recently, Fujimoto and co-workers developed a novel method for the direct synthesis of DMC from methanol and CO₂, using ZrO₂ catalysts to avoid these problems [2].

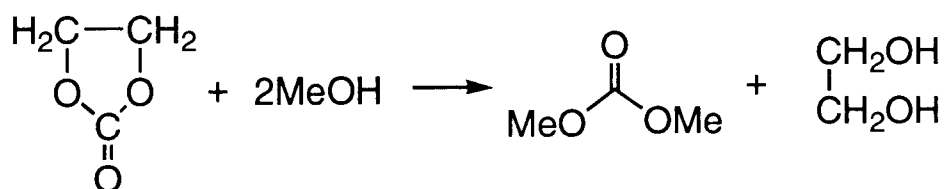
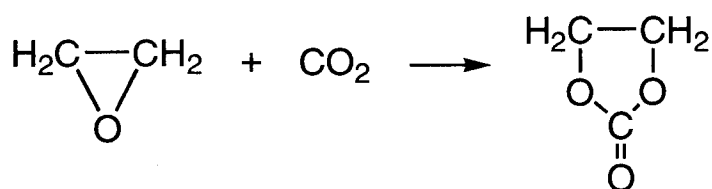
The method for the oxidative carbonylation of methanol to DMC



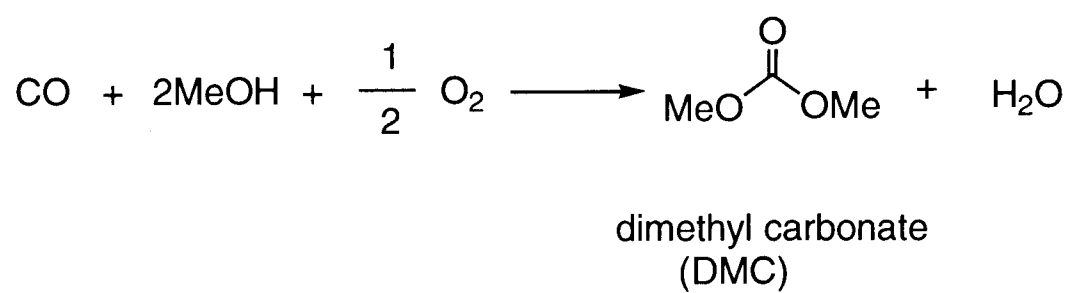
Scheme 1. Application of DMC in chemical industry.



Scheme 2. DMC synthesis from phosgene.



Scheme 3. Transesterification route to DMC.



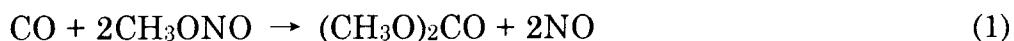
Scheme 4. DMC synthesis by oxidative carbonylation of methanol.

(Scheme 4) is useful and many researchers paid attention to this method. Enichem Synthesis Corporation have succeeded to stage up the original catalytic processes to industrialization.

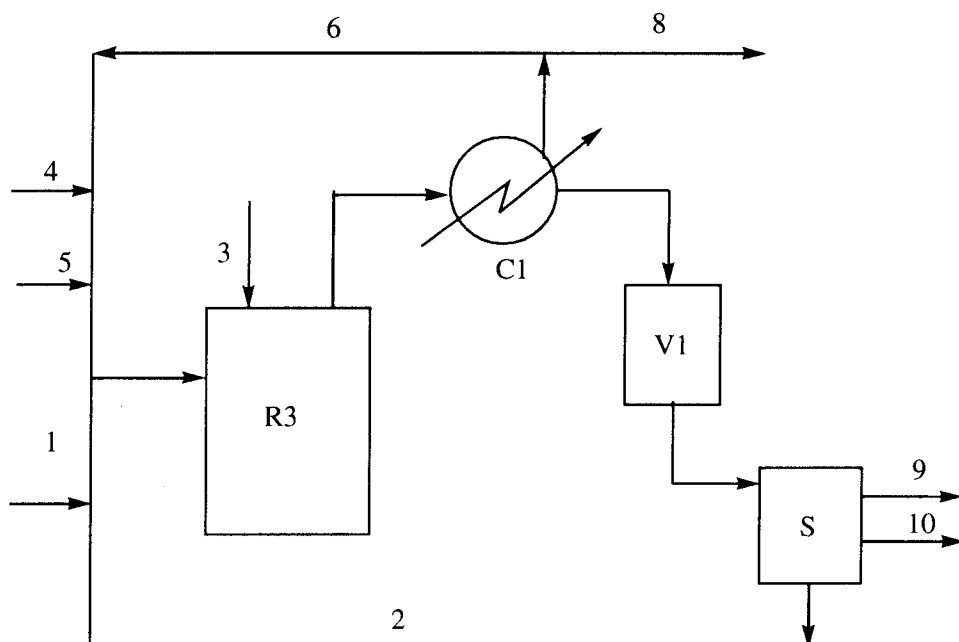
Enichem Synthesis Corporation, a major DMC producer, developed the DMC synthetic process using a slurry CuCl catalyst in the liquid phase (Figure 1(A)) [3]. The high corrosive character of Cl^- required glass-lined equipment. Dangerous explosions initiated by the cracking of the glass suggested the worrisome possibility that the scale of the reactor, which directly affects the productivity of DMC, might have to be restricted.

Several efforts have been made to develop a non-corrosive metal halide catalyst supported by inorganic materials, mainly in the vapor-phase reaction. It has been reported that a CuCl_2 catalyst supported on activated carbon exhibited high activity [4]. However, the loss of Cl^- during the reaction is unavoidable [5] and requires the use of a catalyst regeneration procedure by adding HCl into the reactor, which in turn induces more serious corrosion. A zeolite-supported Cu(I) catalyst prepared by solid-state ion exchange at $650\text{ }^\circ\text{C}$ was recently reported to exhibit high catalytic activity and to be more stable than the activated carbon-supported CuCl_2 catalyst [6].

On the other hand, Ube Industries, Ltd. developed a sophisticated, excellent DMC synthetic process using a supported Pd(II) catalyst with methyl nitrate as a mediator of oxygen. Dimethyl oxalate (DMO) is used to remove methanol from the reaction mixture by absorption (Figure 1(B)) [7].

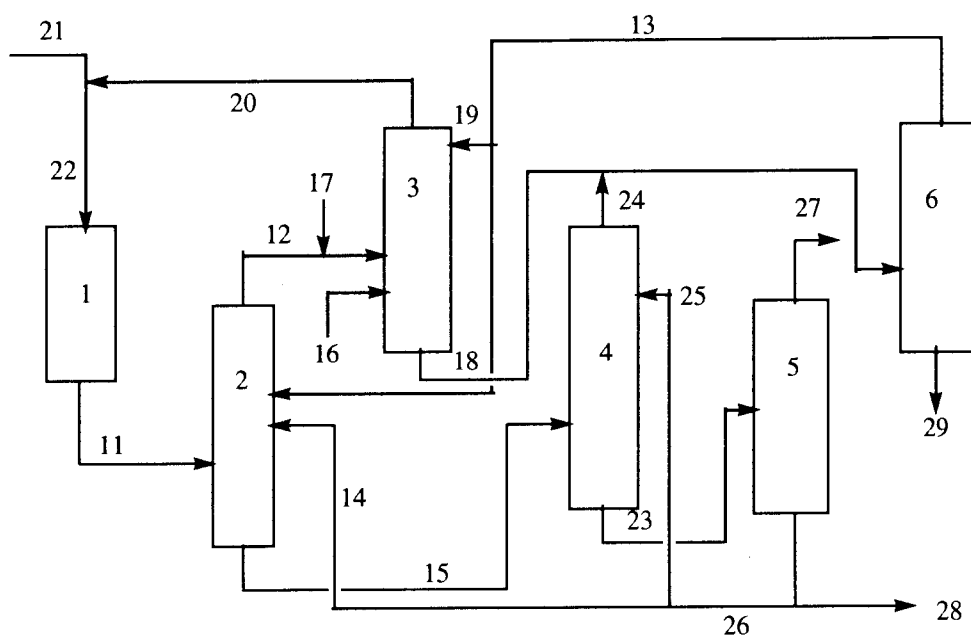


In vapor-phase reactions, unnegligible amounts of methyl formate and methylal were produced as by-products that lower DMC selectivity. In the liquid-phase reaction, these by-products were less, and the overall yield of



R3: reactor, C1: heat exchanger, S: fractional distillation, 1: new MeOH, 2: liquid for recycle, 3: HCl, 4: CO, 5: O₂, 6: gas for recycle, 7: product gas, 8: gas for waste, 9: DMC(product), 10: H₂O(by-product).

Figure 1(A). Enichem DMC processes (JP Patent 5194327).



1: reactor, 2: absorber, 3: regenerator, 4: extractive distillation, 5: distillation, 6: redistillation for MeOH, 11: product gas, 12: gas (CO rich), 13: MeOH, 14: dimethyl oxalate(DMO), 15: DMO+ MeOH, 16: NO_x, 17: NO_x, 18: H₂O, 19: MeOH, 20: recycled CH₃ONO, 21: CO, 22: CO+NO+ CH₃ONO, 23: DMC+DMO, 24: recycled MeOH, 25: DMO, 26: DMO, 27: DMC(product), 28: DMO, 29: liquid for waste.

Figure 1(B). Ube DMC processes (JP Patent 625104).

DMC from methanol was reported to amount up to 95 % in spite of high methanol conversion [8].

Therefore, it is of great value to study non-corrosive immobilized catalysts in the liquid-phase reaction. Until recent years, only poly(4-vinylpyridine) had been studied as a polymer support for CuCl_2 in the liquid-phase DMC synthesis, and moderate catalytic activity and lower corrosive character had been observed [9].

2. Trials to Immobilize Homogeneous Catalysts

Various transition-metal-complex catalyzed homogeneous reactions have been developed, and some of them have been industrially employed. High catalytic activity and selectivity can be attained by designing the catalyst.

However, the separation of the product from the reaction mixture (including the catalyst and the by-product) causes difficulties and requires a considerable amount of equipment and energy. The total industrial process requires complicated separation, purification and catalytic re-generation processes. Additionally, the corrosive character of the catalyst to the reactor material sometimes becomes a serious problem. From these reasons, industrially adopted homogeneous catalytic reactions are considerably fewer than heterogeneous ones.

At present, the molecular design of the ligand for central metals which takes into account its own reaction mechanism, can achieve high catalytic activity because the characterization of the homogeneous catalyst at the molecular level is relatively easier.

Homogeneous catalysts with halogen ligands cause corrosion to the

metallic equipment. Typical examples are the Wacker-type reaction (palladium-copper-chloride catalyst), acetic acid synthesis by the Monsanto process (rhodium-iodide catalyst), and dimethyl carbonate (DMC) synthesis by oxidative carbonylation of methanol (copper-chloride catalyst). To prevent severe corrosion, expensive corrosion-resisting metals such as titanium and zirconium are often used for equipment material. When no metallic materials can be used, glass-lined material becomes necessary.

In order to overcome the disadvantages of homogeneous catalysts. Immobilization of homogeneous catalysts by organic or inorganic support is thought to be effective (Table 1 (A)–(C)). Numerous efforts have been made to immobilize Rh, Ru, and Co catalysts for the hydroformylation reaction (Table 1 (A)) [10]. Loss of expensive metals due to catalytic inactivation is a major problem, and many researchers have tried to develop stable and active immobilized catalysts. Among these catalysts, phosphine-substituted polystyrene [11] has been reported to be an excellent organic support. Poly(4-vinylpyridine) (PVP), one of the most widely used supports [12], suppressed the corrosion of metallic reactors caused by the rhodium-iodide catalyst used in acetic-acid synthesis [13] and by copper-chloride catalyst used in DMC synthesis [14].

Table 1 (A)Immobilization of catalyst for *"Hydroformylation"* reactions.

Substrate	Immobilized Catalyst		
	[p-NaO ₃ SC ₆ H ₄ CH ₂] ₂ C(CH ₂ PPh ₂) ₂ [support]	liquid phase	1)
1-hexene	Rh/C, Co/SiO ₂	liquid phase	2)
	Rh complex/phosphine, amine, vinylpyridine substituted polystyrene	liquid phase	3)
styrene	Rh/SiO ₂	liquid phase	4)
1-heptene	Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈ /Al ₂ O ₃		5)
1-heptene	Ru/rare-earth metal oxide	better than Al ₂ O ₃ support	6)
1-octene	Ru-Co/13X (zeolite)		7)
1-hexene	Ru ₃ (CO) ₁₂ /2,2'-bipyridine/SiO ₂	column reactor, gas phase	8)
	(PPh ₃) ₃ RhH(CO)/Al ₂ O ₃	liquid phase	9)
ethylene	cis-[PtCl ₂ (PPh ₃) ₂], SnCl ₂ /SiO ₂		10)
ethylene	K ₂ [Rh ₁₂ (CO) ₃₀]/SiO ₂ , Al ₂ O ₃ , MgO		11)
	Rh ₄ (CO) ₁₂ /P(CH ₂ OH) ₃ /SiO ₂	gas phase	12)
ethylene	Rh/SiO ₂ , Ni/SiO ₂ , Ru/SiO ₂		13)
1-octene	RhH(CO)[P(C ₆ H ₄ SO ₃ Na-m) ₃] ₃		14)
	Co, Ru, Rh/SiO ₂ , Al ₂ O ₃	in situ with Ph ₃ P	15)
1-pentene	HRh(PPh ₃) ₃ CO/phosphine substituted polystyrene		16)

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Table 1 (B)Immobilization of catalyst for "*Wacker*" reactions.

Substrate	Immobilized Catalyst		
1-butene	Pd/MeHPMoV _x /Al ₂ O ₃ , TiO ₂		1)
1-butene	Pd/H _{3+n} PV _n Mo _{12-n} O ₄₀ /SiO ₂	gas phase	2)
1-butene	Pd/V ₂ O ₅ mono layer/Al ₂ O ₃ , TiO ₂	PdO(active species)	3)
	Cu-Pd-Exchanged Y Zeolites	Cu-O-Pd-O-Cu(active species) electron transfer mediated by H ₂ O	4)
cyclohexene	Pd/C, Pd(II) acetate-hydroquinone- iron phthalocyanine		5)
	Pd/Polybenzimidazol	high heat resistance	6)
1-butene	PdSO ₄ -V(O)SO ₄ -H ₂ SO ₄ /C		7)
ethylene	Pd-Ru-V ₂ O ₅ /α-Al ₂ O ₃	V ⁵⁺ /V ⁴⁺ redox	8)

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Table 1 (C)Immobilization of Rh catalyst for "*Monsanto*" acetic acid synthesis.

Support for Rh		
ion exchange resin	liquid phase	1)
phosphine substituted polystyrene	liquid phase	2)
polyvinylpyridine	liquid phase	3)
H ₃ M ₁₂ PO ₄₀ (M=Cr,Mo,W)	gas phase	4)
The porous carbon composite	gas phase, better than active C	5)
Zeolites X and Y	gas phase, (Si/Al ratio 1.1-100)	6)

- 1) R. S. Drago, et al, Inorg Chem., 20 (1981) 175.
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3. Molecular Design of Polymer-Supported CuCl_2 Catalyst for DMC Synthesis

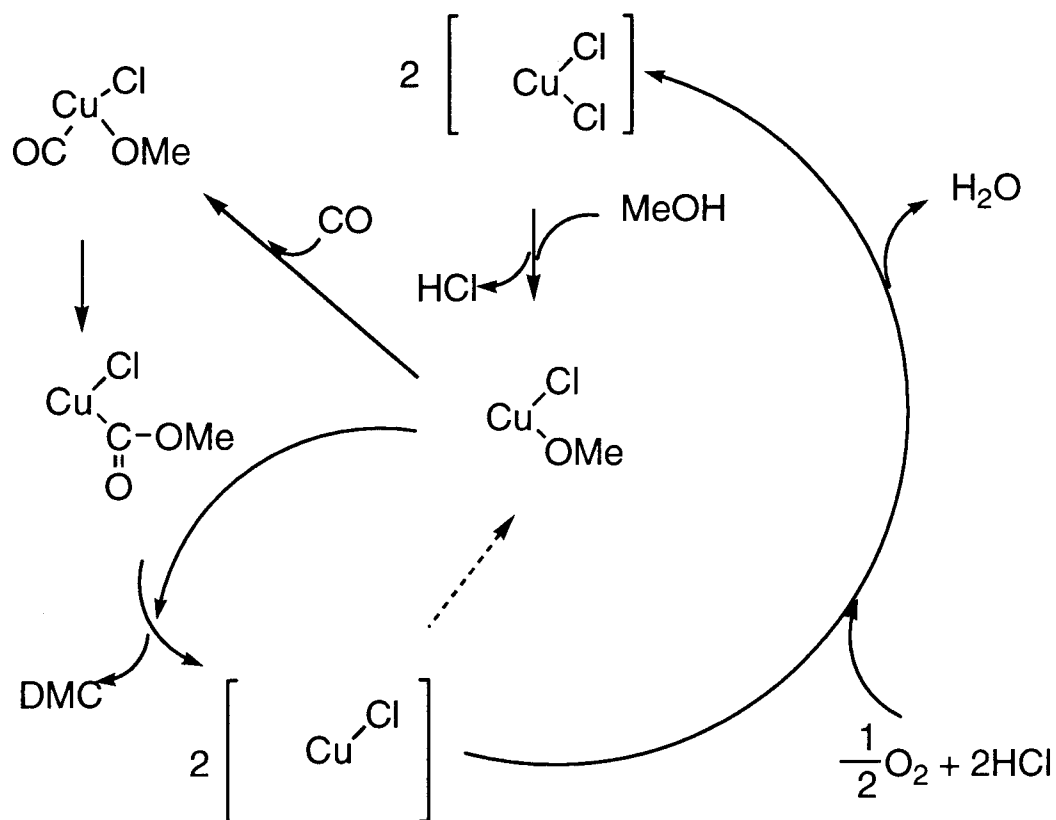
The existence of halide ion under the condition of the redox of copper atom is considered to induce severe corrosion to metallic materials, whose mechanism has been studied [15]. DMC synthesis using CuCl_2 catalyst is promoted by ligand exchange reactions of the central Cu atom shown in Scheme 5. Then, to bind Cu tightly with a chelating bidentate bond is considered to bring about both high stability of the immobilized catalyst and a minor corrosive effect due to Cl^- in the solution. A pyridine unit is advantageous for the coordinating site because the free N site can trap corrosive HCl generated during the reaction as the pyridinium salt.

With this in mind, we designed and selected four polymers, including a 2,2'-bipyridine (bpy) unit, -poly(2,2'-bipyridine-5,5'-diyl) (PBpy), poly(pyridine-2,5-diyl) (PPy), poly(*N,N'*-bisphenylene-2,2'-bipyridine-4,4'-dicarboxylic amide) (Bpya), poly(4-methyl-4'-vinyl-2,2'-bipyridine) (Pvbpy)-, and one chelate compound, 8-quinolinol (oxine) (oxH , $\text{ox} = \text{C}_9\text{H}_6\text{NO}^-$), as supports (or ligands) for CuCl_2 immobilization. Their molecular structures are shown in Scheme 6.

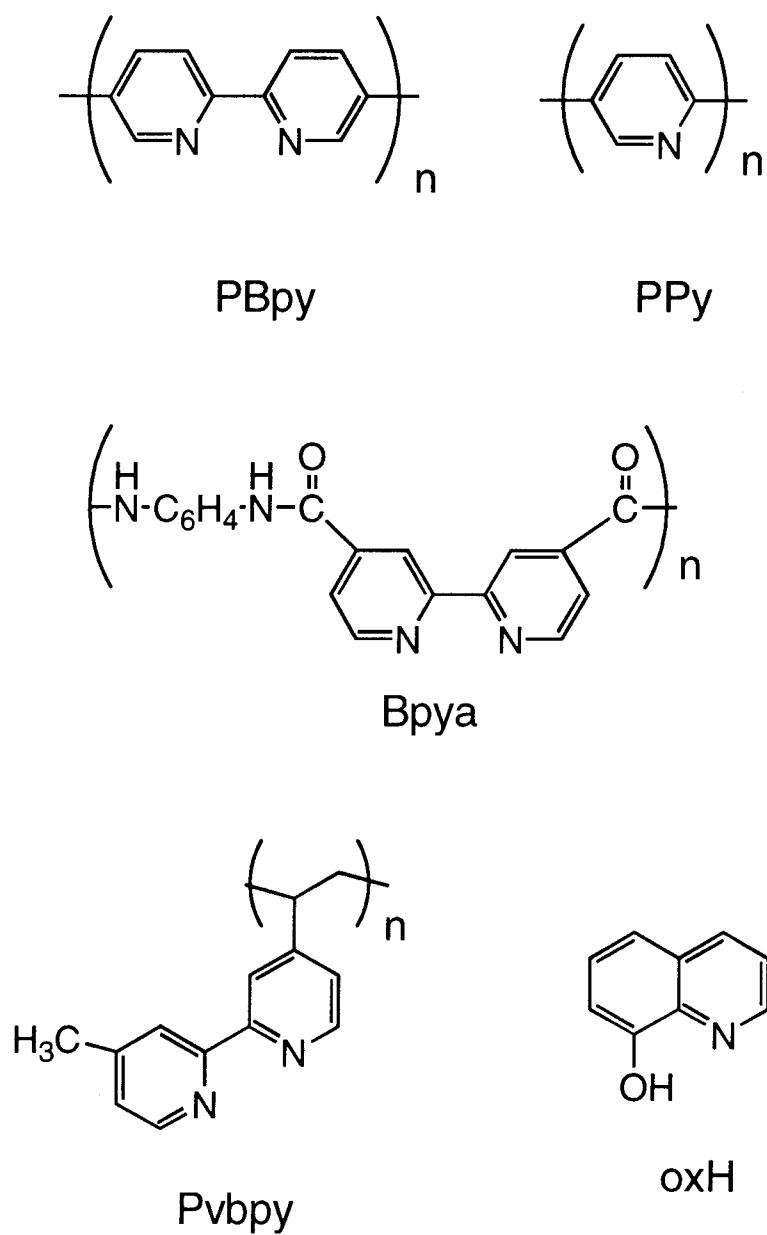
These supports are characteristic as to their different coordination sites (bidentate 2,2'-bipyridine, oxine, and monodentate pyridine), bond types (coordinate, ionic), and polymer types (π -conjugated, aramid, polyvinyl), which are responsible for their own physical properties (stability constant to metals, heat resistance, etc.).

The characteristics and physical properties of the Cu(II) complexes are summarized in Table 2. Except for PPy- CuCl_2 , all the coordination sites of the catalysts are bidentate of bpy or oxine; however, a part of the pyridine unit of PPy was considered to take the head-to-head (bpy like) mode [16]. All the catalysts possess an N-Cu coordination bond.

$\text{Cu}(\text{ox})\text{Cl}$ and $\text{Cu}(\text{ox})_2$ were prepared by ion exchange of Cl^- to ox^- ; thus,



Scheme 5. Plausible reaction mechanism including Cu(II)/Cu(I) redox cycles.



Scheme 6. Molecular structures of supports (ligands).

the atomic ratios of Cl/Cu are 1 and 0, respectively, which are lower than those of the other polymer-supported catalysts in Table 2.

The stability constant to Cu(II) ($\log K$) [17] of bpy is higher than that of pyridine due to its chelation, while oxine is known to make an extremely stable complex with Cu(II).

The Cu(II) coordination ratios per coordination site were obtained from the elemental analysis of Cu by X-ray fluorescence spectrometry (XRF). The values of PBpy-CuCl₂, Bpya-CuCl₂, and Pvbpy-CuCl₂, whose coordination sites is bpy, are around 70–80 mole%. In contrast, PPy, whose coordination site is pyridine exhibits the value of 40 mole%. This indicates that two pyridine units in the PPy-polymer participate in the coordination to one Cu atom (including intermolecular and intramolecular (bidentate) coordinations), and the remaining 20 % of the pyridine unit exists as a free ligand, on average.

PBpy and PPy are polymers that have expanded the π -conjugation system. Bpya is an aromatic polyamide (aramid). These types of π -conjugated polymers [16] and aramid polymers [18] are known to show high heat resistance. The melting point of the above three polymers was confirmed to be >250 °C, which may be due to their rigid, rod-like structures. High heat resistance is one of the important characteristics a catalyst must have to give high catalytic stability. The bpy unit of Pvbpy exists in the side chain of the polymer (polyvinyl-type), showing a lower melting point of 165 °C.

The higher coordination ratio of Pvbpy-CuCl₂ compared to those of PBpy-CuCl₂ and Bpya-CuCl₂ may be due to the more flexible bpy unit in the polymer. The degrees of polymerization of these polymers were estimated (Table 2).

MOPAC molecular orbital (MO) calculations were performed at the PM3 level of theory to elucidate the coordination abilities of pyridine, 2,2'-bipyridine, and 8-quinolinol. As shown in Figure 2, the next highest

Table 2

Characteristics and physical properties of the Cu(II) catalysts.

Catalyst	Coordination site	Bond type	$\log K^a$	Cu(II) occup. at coord. site	Polymer type	Mp ^b	Degree of polymerization ^c
PBpy-CuCl ₂	bpy	coordinate	6.4 ^d	72%	π -conjugated	>250	10
PPy-CuCl ₂	pyridine	coordinate	4.5 ^e	40%	π -conjugated	>250	26
Bpya-CuCl ₂	bpy	coordinate	6.4 ^d	77%	aramid	>250	15
Pvbpy-CuCl ₂	bpy	coordinate	6.4 ^d	82%	polyvinyl	165	26
Cu(ox)Cl	oxine	coordinate + ionic	13.5 ^d	~100%	-	74	-
Cu(ox) ₂	oxine	coordinate + ionic	171.7 ^e	~50%	-	74	-

^a Stability constant of the coordinating site as a molecule (bpy, pyridine, oxine) measured in aqueous solution at room temperature (Ref. [17]).

^b Melting point (°C) of the support (ligand). ^c 'n' in scheme 6.

^d $K = [\text{MA}]/[\text{M}] [\text{A}]$. ^e $K = [\text{MA}_2]/[\text{M}] [\text{A}]^2$ (M: Cu²⁺, A: coordination site).

occupied MOs (HOMO-1) of the ligands are important for coordination with Cu^{2+} . By the perturbation theory, the orbital interaction energy between the HOMO-1 of the ligands and the lowest unoccupied (LU) MO of Cu^{2+} is estimated by the following equation:

$$\Delta E = 2C_a^2 C_b^2 \beta^2 / |E_b - E_a| ,$$

where β is the resonance integral and E_a and C_a^2 are the HOMO-1 energy and square of the HOMO-1 coefficient of the ligands, respectively, and E_b and C_b^2 are the LUMO energy and square of the LUMO coefficient of Cu^{2+} , respectively. According to the equation, ΔE becomes larger with increasing E_a and/or increasing C_a^2 , assuming that β , E_b , and C_b^2 are independent of the kind of ligand. In Table 3, the calculated HOMO-1 energies E_a (eV) and squares of the HOMO-1 coefficients (C_a^2) of the ligands are listed. E_a of 2,2'-bipyridine is larger than that of pyridine (the absolute value of E_a of 2,2'-bipyridine is smaller than that of pyridine.), and C_a^2 of 2,2'-bipyridine is also larger than that of pyridine. Therefore, the stabilization constant K between 2,2'-bipyridine and Cu^{2+} is expected to be larger than that between pyridine and Cu^{2+} .

This estimation is in accordance with the experimental fact previously shown in Table 2: $\log K(2,2'\text{-bipyridine}) > \log K(\text{pyridine})$. K of 8-quinolinol is larger than that of either pyridine or 2,2'-bipyridine. This experimental fact is also explained by the orbital interaction concept; E_a of 8-quinolinol is much larger than that of either pyridine or 2,2'-bipyridine, and this factor probably contributes mainly to the stabilization of a coordination bond between 8-quinolinol and Cu^{2+} , although C_a^2 of 8-quinolinol is smaller than that of either pyridine or 2,2'-bipyridine.

As described above, the physical properties of these immobilized catalysts are different in each case, according to the parameters outlined in Table 2. In the following sections, we will clarify the effects of these

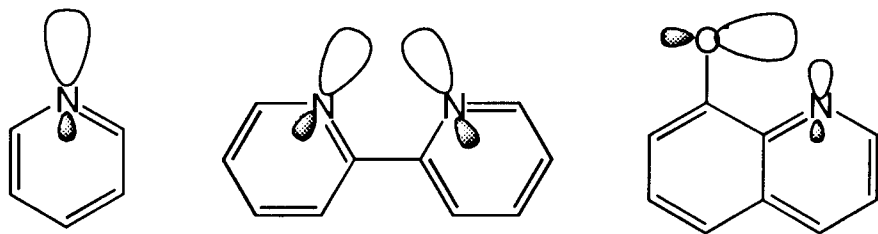


Figure 2. HOMO-1 of pyridine, 2,2-bipyridine, 8-quinolinol

Table 3

The values of E_a , C_a^2 of pyridine, 2,2'-bipyridine, 8-quinolinol

	pyridine	2,2'-bipyridine	8-quinolinol
$E_a(\text{eV})$	-10.199	-10.030	-5.342
$C_a^2(C_a^2 \sim C_{as}^2 + C_{ap}^2)$	0.735	0.739	0.699

C_{as} and C_{ap} are coefficients of s and p orbitals.

parameters in the DMC synthesis by comparing their own catalytic behaviors.

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Chapter 2

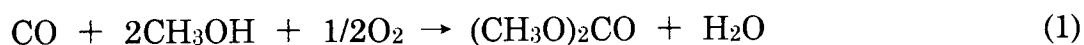
Synthesis of DMC by Oxidative Carbonylation of Methanol using Poly(4-methyl-4'-vinyl-2,2'-bipyridine)-Supported CuCl₂ Catalyst

ABSTRACT

Polymer, including 2,2'-bipyridine, poly(4-methyl-4'-vinyl-2,2'-bipyridine) (Pvbpy), was investigated for the synthesis of dimethyl carbonate (DMC) as a support for CuCl₂, by oxidative carbonylation of methanol in the liquid-phase. The CuCl₂ complex (Pvbpy-CuCl₂) was insoluble in methanol, and the reaction system was heterogeneous. The Pvbpy-CuCl₂ catalyst showed considerable catalytic activity (DMC yield: 44.4 % and DMC selectivity: 92.6 %, at methanol conversion: 1.79 %), which is comparable to the previously reported data of poly(4-vinylpyridine) (PVP)-CuCl₂ catalyst; the Pvbpy-CuCl₂ catalyst could be recycled after filtration and washing thrice, provided, not having lost activity. The corrosion originating from Cl⁻ was greatly improved by immobilizing the CuCl₂ by Pvbpy. Elimination of CuCl₂ from the Pvbpy support was observed during the reaction. In the first reaction, about 38 % of the initially supported Cl was released, and in the second and the third reactions, most of the Cl was kept. The rate of corrosion of stainless steels in the first use of the catalyst was greater than that in the rate of the second and the third uses. These results are closely related to the amount of Cl⁻ released from the Pvbpy support, which demonstrates that the main cause of corrosion in the catalytic system is Cl⁻ released from the Pvbpy-CuCl₂ catalyst. From XPS study of the catalyst, it became obvious that Cu(II) was gradually reduced to Cu(I) during the reaction.

1. INTRODUCTION

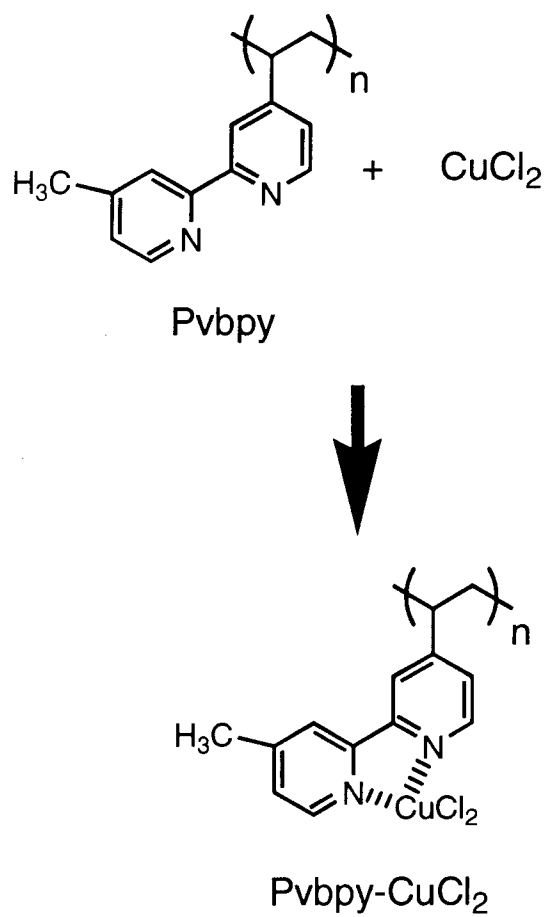
Dimethyl carbonate (DMC) is a promising commodity, and a chemical compound from the viewpoint of environmental problem, world-wide. DMC is useful as an organic solvent and a fuel additive, for many purposes. Additionally, it is likely to replace toxic COCl_2 which is widely used as a starting material of polycarbonate. The method of oxidative carbonylation of methanol (Eq. (1)) by CuCl catalyst, which is practiced in the industry, is useful to produce DMC [1]. The catalyst, however, rapidly loses activity by releasing Cl^- during the reaction. The process is slurry liquid-phase, being severely corrosive to many metals. Thus, glass lining is necessary to protect the inside of the reactor. CuCl_2 which is soluble in methanol, is also known as effective catalyst for DMC synthesis [2], although, it also has corrosive properties.



Attempts to immobilize copper chloride to organic or inorganic supports were made. Activated carbon [3], Y type zeolite [4] is reported to be useful in the gas-phase reaction. The heterogenized catalysts, including pyridine ring in their supports as a coordinating site to Cu, are expected to achieve high catalytic activity in the liquid-phase reaction.

On the other hand, 2,2'-bipyridine was widely studied, including Ru(II) complexes in the areas of photochemistry and electrochemistry [5]. Poly(4-methyl-4'-vinyl-2,2'-bipyridine) (Pvbpy) is a polymer, including 2,2'-bipyridine unit and also studied concerning the photochemical and electrochemical properties of its Ru(II) complex, and was expected to become a new material for solar cells [6].

We first synthesized the Pvbpy- CuCl_2 complex and found that Pvbpy is useful as a support for CuCl_2 , and also that the CuCl_2 complex (Scheme 1) is



Scheme 1. Immobilization of CuCl₂ by Pvbpy support.

active as a heterogenized catalyst for the synthesis of DMC. The Pvbpy-CuCl₂ catalyst showed high reaction activity and less corrosiveness to stainless steels, and that it could be easily recycled after filtration.

2. EXPERIMENTAL

2.1. Synthesis of Pvbpy-CuCl₂

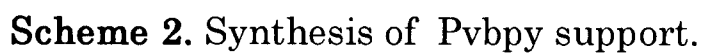
Pvbpy was synthesized by typical procedure described in the literature [7] (Scheme 2).

Synthesis of 4,4'-Dimethyl-2,2'-Bipyridine mono-N-Oxide

To 4,4'-dimethyl-2,2'-bipyridine (500 g: 2.72 mol) and CHCl₃ (5.6 L) in a 10 L reactor, m-chloroperbenzoic acid was added at cooled in an ice-bath, and the mixture was stirred for 1 h and then for 24 h at room temperature. Saturated NaHCO₃ aqueous solution (4 L) was added to the reaction mixture at cooled in an ice-bath, and the mixture was stirred. The organic layer was washed by saturated NaHCO₃ aq. 3 times and dried over MgSO₄, and the solvent was evaporated. 4,4'-dimethyl-2,2'-bipyridine (489 g: 2.66 mol) and m-chloroperbenzoic acid (626 g: 3.63 mol) were used for the second batch reaction. A total of 4,4'-dimethyl-2,2'-bipyridine mono-N-oxide (935 g: 70 % purity) was obtained.

Synthesis of 4-Chloromethyl-4'-Methyl-2,2'-Bipyridine

p-Toluenesulfonyl chloride (224 g: 1.18 mol) in anhydrous dioxane (1 L) was added to 4,4'-dimethyl-2,2'-bipyridine mono-N-oxide (70 % purity; 286 g: about 1.00 mol) and anhydrous dioxane (2 L) in a 5 L reactor during a period



of 2 h under reflux. The reaction mixture was stirred for 3 h and cooled to room temperature. 5 % HCl (1 L) was added to the mixture, and this was washed with toluene. Aqueous NaOH was added to the mixture until pH = 10. This was extracted by CHCl₃ and dried over MgSO₄, and CHCl₃ was evaporated. 4,4'-dimethyl-2,2'-bipyridine mono-*N*-oxide (70 % purity; 615 g: about 2.15 mol) and p-toluenesulfonyl chloride (482 g: 2.53 mol) were used for the second batch reaction. A total of 4-chloromethyl-4'-methyl-2,2'-bipyridine (940 g: 45 % purity) was obtained.

Synthesis of 4-(Methylenetriphenylphosphonium)-4'-Methyl-2,2'-Bipyridine Chloride

4-Chloromethyl-4'-methyl-2,2'-bipyridine (45 % purity; 910 g: about 1.87 mol), triphenylphosphine (604 g: 2.31 mol), and anhydrous toluene (8 L) were refluxed for 23 h. The reaction mixture was cooled to room temperature, and the obtained precipitate was filtered, washed with toluene, and dried; 4-(methylenetriphenylphosphonium)-4'-methyl-2,2'-bipyridine chloride (310 g) was obtained (yield, 34.5 %).

Synthesis of 4-Vinyl-4'-Methyl-2,2'-Bipyridine

To p-formaldehyde (880 g: 29.3 mol), anhydrous methanol (5 L) in a 10 L reactor, 0.70 M KOMe/MeOH (330 ml) was added at room temperature, and the mixture was stirred for 30 min. 4-(methylenetriphenylphosphonium)-4'-methyl-2,2'-bipyridine chloride (270 g: 0.561 mol) and 0.70 M KOMe were added to the reaction mixture as the MeOH solutions during a period of 75 min, and the reaction mixture was stirred for 3 h; the solvent was then evaporated. The residue was purified by a silica gel column (CHCl₃, followed by ethyl acetate/hexane = 1/50, using aminated silica gel) to obtain 35 g of 4-vinyl-4'-methyl-2,2'-bipyridine (purity, >98 %; yield, 31.8 %).

Synthesis of Poly(4-Vinyl-4'-Methyl-2,2'-Bipyridine)

Argon gas was poured into 4-vinyl-4'-methyl-2,2'-bipyridine (30 g: 0.153 mol), anhydrous toluene (150 ml) in a 300 ml reactor during a period of 40 min. The mixture was heated to 65 °C, and AIBN (70.2 mg) in anhydrous toluene (10 ml) was added to the mixture. This was stirred for 60 h. The reaction mixture was poured into ether (1.5 L) and stirred for 30 min. The obtained Poly(4-vinyl-4'-methyl-2,2'-bipyridine) was filtered off and dried (yield, 92.7 %; 27.8 g, white powder). Found to contain: C, 80.2; H, 6.02; N, 13.63 %. Calcd. as C₁₃H₁₂N₂: C, 80.2; H, 6.16; N, 14.02 %. From GPC measurement: Mn/Mw was estimated to be 2700/5100.

Pvbpy was dissolved in 50 % CH₂Cl₂/methanol at room temperature, and 2 equimolecular amount of CuCl₂ in methanol was gradually added to the Pvbpy solution, while stirring vigorously, and the mixture was refluxed for 5 h. The Pvbpy-CuCl₂ complex was precipitated as green powder which was not soluble in methanol.

From the elemental analysis of Cu by X-ray fluorescence spectrometer (XRF) of the obtained complex (18.6 wt%), it was calculated that 82 mole% of bipyridyl unit was coordinated to CuCl₂. A X-ray diffraction (XRD) measurement was made for the Pvbpy-CuCl₂ catalyst and no peak was detected. This might indicated that the Cu species were highly dispersed on the support (Figure 1).

2.2. Synthesis of CuCl₂ Complex with PS-Cy

PS-Cy was synthesized by typical procedure described in the literature [8] (Scheme 3).

Synthesis of Chloromethylated Polystyrene

Polystyrene (PICCOLASTIC D125) (50 g) was dissolved to chloromethyl

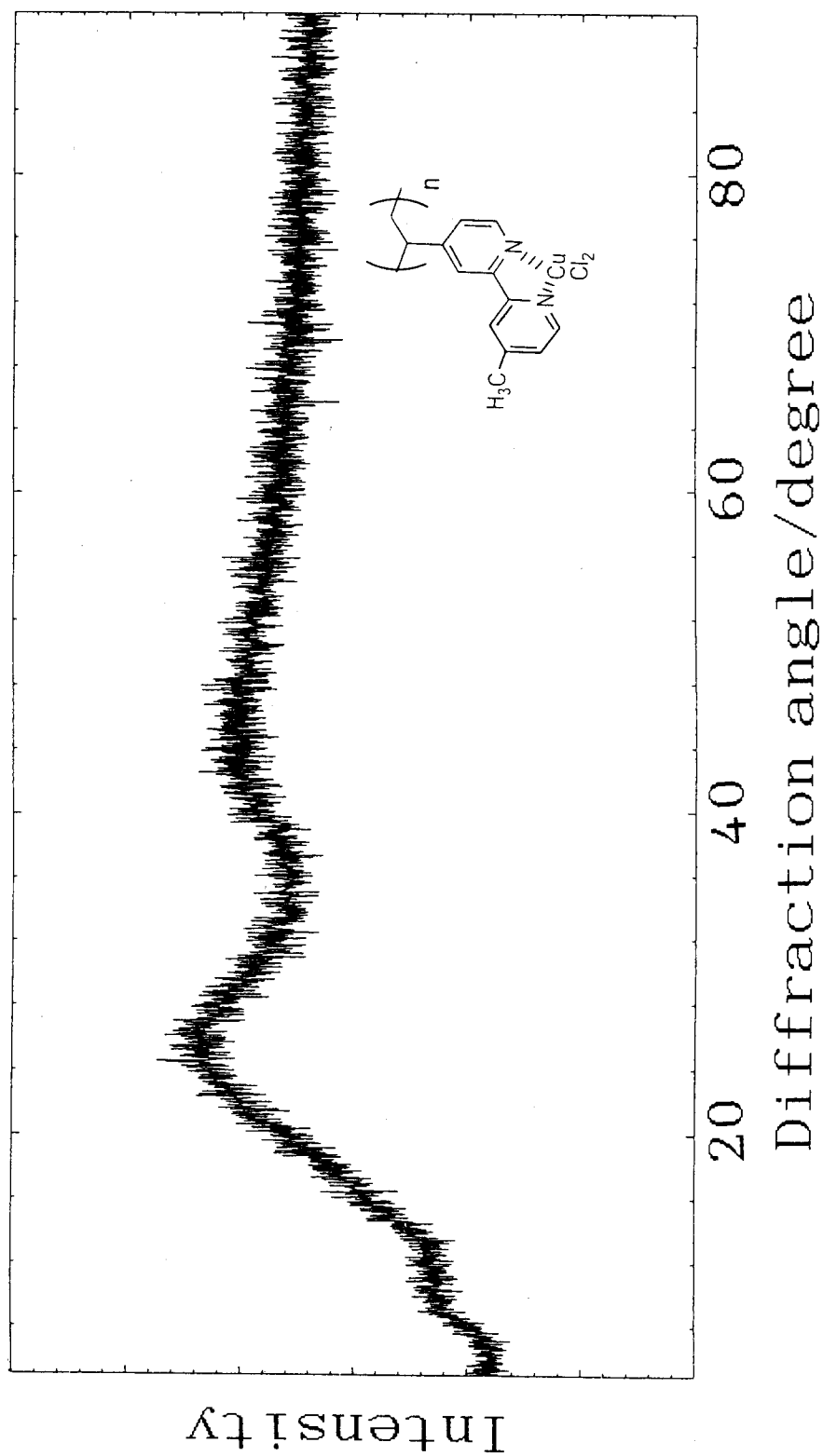
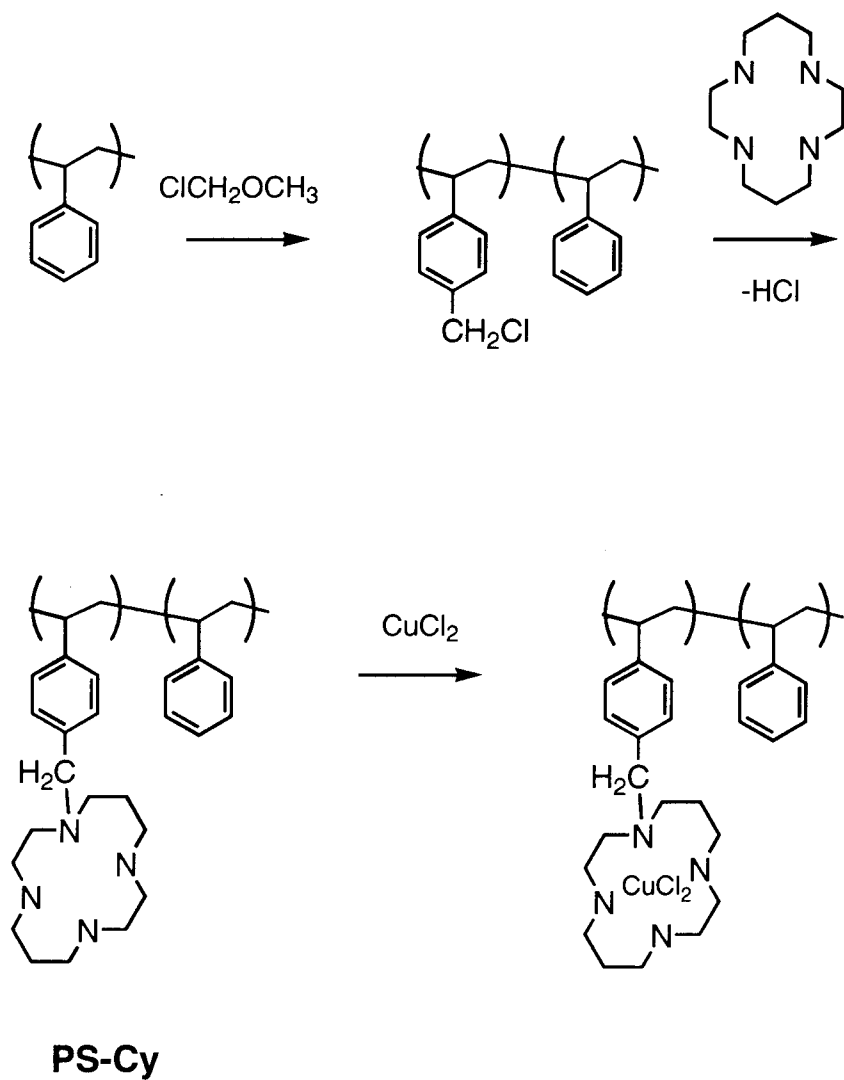


Figure 1. XRD spectra of Pvbpy-CuCl₂. X-ray source was Cu K α .

The sample was measured under atmospheric pressure.



Scheme 3. Synthesis of PS-Cy and the CuCl_2 complex.

methyl ether (300 ml) in a 2 L reactor. Dichloromethane (600 ml) and ZnCl_2 (8.1 g) were added to the solution at cooled in an ice-bath, and the mixture was stirred for 2.5 h and then for 48 h at room temperature. 2 N HCl (100 ml) was added to the mixture at cooled in an ice-bath, and the mixture was stirred for 30 min. The solution was transferred into a separatory funnel together with chloroform/water. The extracted organic (chloroform) layer was washed with water and dried over MgSO_4 , and chloroform was evaporated. Chloromethylated polystyrene (68 g) was obtained as white powder. From the elemental analysis data (C, 75.5; H, 6.6; Cl, 12.5 %), it was calculated that 44.4 % of the benzene ring was chloromethylated.

Synthesis of Cyclam (1,4,8,11-Tetraaza-cyclododecane) Substituted Polystyrene (PS-Cy)

Chloromethylated polystyrene (60 g), cyclam (55 g: 0.275 mol), and chloroform (1.2 L) were introduced into 2 L reactor, and the mixture was stirred for 110 h at room temperature. The solvent was evaporated, and the residue was washed with dilute HCl aq., water, dilute NaOH aq., and water (in this order), and dried in vacuum. PS-Cy (51.2 g) was obtained as a white powder. It was calculated from the elemental analysis data (C, 81.8; H, 8.7; N, 9.2; Cl, 0.09 %) that 26.4 % of the benzene ring was substituted by cyclam. The Cl % was extremely low in spite of such a low substituted ratio (26.4 %). We thought that a portion of the used polystyrene, which had lower molecular weight, was highly chloromethylated and substituted by cyclam; this was washed off when the excess cyclam was removed. An equimolar amount of CuCl_2 to cyclam in PS-Cy was gradually added to PS-Cy in methanol. The CuCl_2 complex was precipitated. Found: Cu, 7.7 %; Cl, 9.0 %. Calculated for the 1:1 complex: Cu, 8.6 %; Cl, 9.6 %.

2.3. Synthesis of DMC

Synthesis of DMC was performed according to the following method. In a 30 ml Hastelloy C (HC) 276 autoclave (Cr: 16 %, Mo: 16 %, Fe: 5 %, C: 0.01 %, Ni: base) made by Mitsubishi Material, 10 ml (7.75 g) of methanol as both a substrate and a solvent were introduced and Pvbpy-CuCl₂ powder (457 mg) was added ([Cu] = 150 mM), and CO 23 kgf/cm², O₂ 2 kgf/cm² were introduced to the vapor phase. After reaction at 140 °C for 2 h, the concentrations of DMC, methanol, CO₂, and O₂ were analyzed by gas chromatography; CH₃OH conversion (%) (= produced DMC/(introduced CH₃OH/2)), DMC yield (%) (= produced DMC/(introduced O₂ × 2)), and DMC selectivity (%) (= DMC/(DMC + CO₂)) were calculated. In the DMC synthesis, the reaction mixture was stirred vigorously (~800 rpm) to minimize the diffusion-controlled influence to the DMC yield and selectivity.

The extent of corrosion caused by each catalyst was measured separately according to following method. The test pieces (about 15 mm × 6 mm × 2 mm) of SUS316 (Cr: 18 %, Mo: 2 %, Ni: 10 %, C: 0.08 %, Fe: base, 2.0 ± 0.2 g) and HC276 (3.0 ± 0.3 g) were placed in the reactor. Reaction time was 2 h for each run. The weight of test pieces was measured after the first reaction and the third reaction. The extent of corrosion [mg h⁻¹] is expressed in terms of decrease of the weight of the test pieces.

2.4. XPS Measurement

X-ray photoelectron spectra of the Pvbpy-CuCl₂ catalyst were measured (after preparation (before the reaction) and after the third reaction) with PHYSICAL ELECTRONICS PHI5800 ESCA System (AlK α radiation, 14 kV, 150 W). The compounds in powder form were used and were dusted on both-side adhesive tape and mounted on a sample holder. C(1s)

photoelectron line at 285.0 eV was used as standard.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity

The catalytic activity of the Pvbpy-CuCl₂ catalyst in the synthesis of DMC was studied by oxidative carbonylation of methanol in the liquid-phase. The methanol conversion, DMC yield, and DMC selectivity are listed in Table 1 (Pvbpy-CuCl₂ (1)). In the condition of this reaction, no by-product, excepting CO₂ was detected. The DMC selectivity was thus calculated as DMC/(DMC + CO₂). The reaction was performed at methanol conversion of about 2~3 %, which is lower than the generally reported condition in the continuous flow process (about 5 %) [4].

The Pvbpy-CuCl₂ catalyst could be recycled after filtration and washing with methanol. The loss of weight of the catalyst, attributed to handling during the above procedure, was compensated by adding the fresh catalyst for adjustment, [Cu] = 150 mM. The data of Pvbpy-CuCl₂ (1)~(3) in Table 1 show the catalytic activities of the Pvbpy-CuCl₂ catalyst for the stepwise 3 reactions after the process of filtration and washing. During the 3 recycle processes (total reaction time: 6 h), deactivation of the catalyst observed was almost none.

The data of the poly(4-vinylpyridine) (PVP)-CuCl₂ catalyst which was insoluble in methanol, the 2,2'-bipyridine (Bpy)-CuCl₂ catalyst and the CuCl₂ catalyst which were soluble in methanol, are also listed in Table 1.

Usually, the catalytic activity deteriorates, caused by the immobilization of homogeneous catalyst, as the reaction rate is governed by

the diffusion to the active site in catalyst to encounter the substrate. The DMC yield and selectivity of the PVP-CuCl₂ catalyst were, thus, obviously lower than those of the homogeneous CuCl₂. The DMC yield and selectivity of reaction over the Pvbpy-CuCl₂ catalyst were also lower than those over the homogeneous CuCl₂ catalyst for the same reason.

A part of the Bpy-CuCl₂ complex was precipitated in methanol at room temperature, when equimolar amounts of Bpy and CuCl₂ were added to the reactor as Bpy-CuCl₂ catalyst. The Bpy-CuCl₂ catalyst, however, is considered to be almost homogeneous at the reaction temperature of 140 °C, because the DMC yield and selectivity attained were comparable to those of homogeneous CuCl₂ (Table 1), and the severe corrosiveness to stainless steels was observed (Bpy-CuCl₂ in Table 2). Thus, it became clear that Bpy itself was not a useful support for CuCl₂ in the reaction.

Cyclam binds Cu²⁺ very strongly ($\log K = 25$ [9]); thus, PS-Cy was expected to show good performance as a polymer-support for CuCl₂. However, no DMC or CO₂ was produced using the CuCl₂ complex as an immobilized catalyst. The reason for this could not be clarified, as we did not investigate or analyze this catalytic system more thoroughly. For the stainless test piece which was introduced in the reactor during the above reaction, severe corrosion (which was not estimated quantitatively) was observed. When Cu²⁺ is coordinated to cyclam, the counter anion is placed at the axial space of Cu²⁺ and can easily receive the ligand exchange reaction [10]. We consider that the immobilized Cl⁻ was immediately exchanged to another ligand (like MeO⁻) under the reaction condition and was not able to interact with the supported Cu²⁺, which resulted in the absence of catalytic activity.

Table 1

Catalytic activity of Pvbpy-CuCl₂ comparing to Bpy-CuCl₂ and homogeneous CuCl₂^a.

Catalyst	CH ₃ OH conv. ^b	DMC yield ^c	DMC sel. ^d
Pvbpy-CuCl ₂ (1) ^e	1.79	44.4	92.6
Pvbpy-CuCl ₂ (2) ^e	1.83	45.5	90.4
Pvbpy-CuCl ₂ (3) ^e	2.10	52.2	92.7
PVP-CuCl ₂	1.84	47.1	91.4
Bpy-CuCl ₂	2.92	70.4	95.8
CuCl ₂	2.76	70.0	97.4

^a [Cu] = 150 mM, CH₃OH = 10 ml, CO = 23 kgf/cm², O₂ = 2 kgf/cm²,

Temp. = 140°C, Reaction time = 2 h.

^b CH₃OH conv. (%) = produced DMC/(introduced CH₃OH/2).

^c DMC yield (%) = produced DMC/(introduced O₂x2).

^d DMC sel. (%) = DMC/(DMC + CO₂).

^e (1) ~ (3) represents the recycled use (1st reaction~3rd reaction) of the catalyst.

3.2. Rate of Corrosion

Cl^- in the solution was considered as the main cause of corrosion of stainless steels. Thus, maintaining the immobilization of Cl^- was thought to be effective for decreasing the corrosiveness.

The rate of corrosion measured after the 1st and the 3rd reaction using the Pvbpy- CuCl_2 catalyst, and those of the Bpy- CuCl_2 catalyst and the homogeneous CuCl_2 catalyst as references, are listed in Table 2. The total test period for each data is 2~4 h, and from the limit of the used balance, the range of error was estimated to be about 0.1 mg h^{-1} . Both the homogeneous CuCl_2 and the Bpy- CuCl_2 catalysts showed very high corrosiveness to SUS316 and HC276. On the other hand, the Pvbpy- CuCl_2 catalyst showed good corrosion resistance toward HC276 and SUS316 (Pitting, however, was observed on the surface of metals). For homogeneous reaction, including halogen ion in the catalyst, it was reported that severe corrosion attributed to halogen ion can be considerably prevented by immobilizing the catalyst [11]. In this regard, therefore, Pvbpy is a good support for corrosive CuCl_2 catalyst.

In our experiment, the Pvbpy- CuCl_2 catalyst showed considerable catalytic activity as a heterogenized catalyst for the synthesis of DMC and the corrosiveness of Cl^- was reduced remarkably. Additionally, the recycled catalyst showed less corrosiveness than that of the virgin catalyst.

3.3. Elimination of CuCl_2 from Pvbpy

The ratio of CuCl_2 coordinated to Pvbpy was calculated before the reaction (0 h), after the 1st reaction (2 h) and after the 3rd reaction (6 h) [() total reaction time] from the elemental analysis of Cu and Cl by XRF. The results are shown in Figure 2. 82 mole% of CuCl_2 was coordinated to the

Table 2

The rate of corrosion attributed to Cl^- for Pvbpy- CuCl_2 , comparing with Bpy- CuCl_2 and homogeneous CuCl_2 ^a.

Catalyst	Rate of corrosion/ mg h^{-1}	
	SUS316 ^b	HC276 ^b
Pvbpy- CuCl_2 1st reaction	1.6	0.6
recycled (3rd reaction)	0.4	<0.1 ^c
Bpy- CuCl_2	27.3	4.0
CuCl_2	39.6	8.3

^a Used a test piece with dimensions of 15 mm × 6 mm × 2 mm.

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

^c Within the limit of detection.

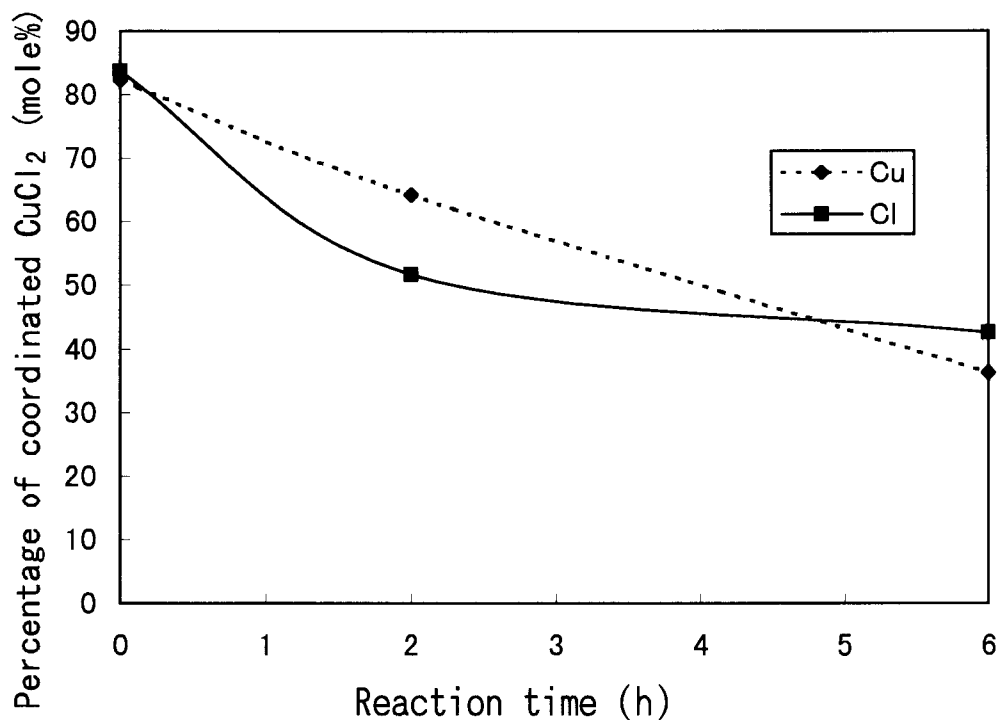
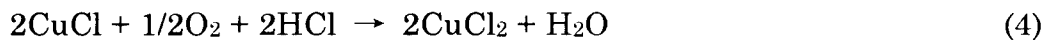
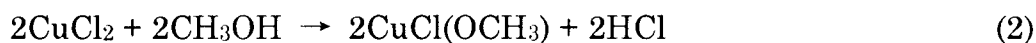


Figure 2. The trend of CuCl_2 elimination from Pvbpy, calculated from Cu, Cl contents in Pvbpy- CuCl_2 .

Reaction Conditions: the same as in Table 1.

Pvbpy support before the reaction. Cu was released gradually from the support, during the reaction (0~6 h). The amount of Cl decreased from 82 mole% to 52 mole% in the first reaction (0~2 h). In the second and the third reactions (2~6 h), however, most of the Cl in the catalyst was maintained. This is closely related to the corrosion ratio (Table 2) of the Pvbpy-CuCl₂ catalyst (1st reaction > recycled). Thus, the main cause of corrosion could be attributed to the Cl⁻ released from the Pvbpy support.

A reaction mechanism, in which the redox of Cu(II)/Cu(I) plays an important role, was proposed for the synthesis of DMC, using copper chloride catalyst (Eq. (2)~(4)) [12].



CuCl(OCH₃) is considered to be the active species [12]. If all of Cu and Cl are coordinated by the 2,2'-bipyridyl unit as CuCl₂, each coordination ratio calculated from Cu and Cl might coincide. This is not in the case (Figure 2), however. It is indicated, from the data, that some ligands of Cu are exchanged from initial Cl⁻ to other groups, such as CuCl(OCH₃), CuCl(OH), etc.

From the XPS measurement of the Pvbpy-CuCl₂ catalyst, it is indicated that reduction of Cu(II) took place during the reaction. Cu(2p 3/2) photoelectron transitions of the Pvbpy-CuCl₂ catalyst after preparation (before the reaction) were observed at 935 eV, with a shoulder peak at 933 eV (Figure 3 (a)). The peak of 935 eV was assigned to CuCl₂ [13], and CuCl, Cu, Cu₂O were reported to show a peak of around 933 eV [13]. The intensities of the two peaks were inverted after the third reaction (Figure 3 (b)). Obviously, the reduction of coordinated CuCl₂ proceeded during the reaction. The ratio of Cu(II)/Cu(I) was estimated from the summation of the

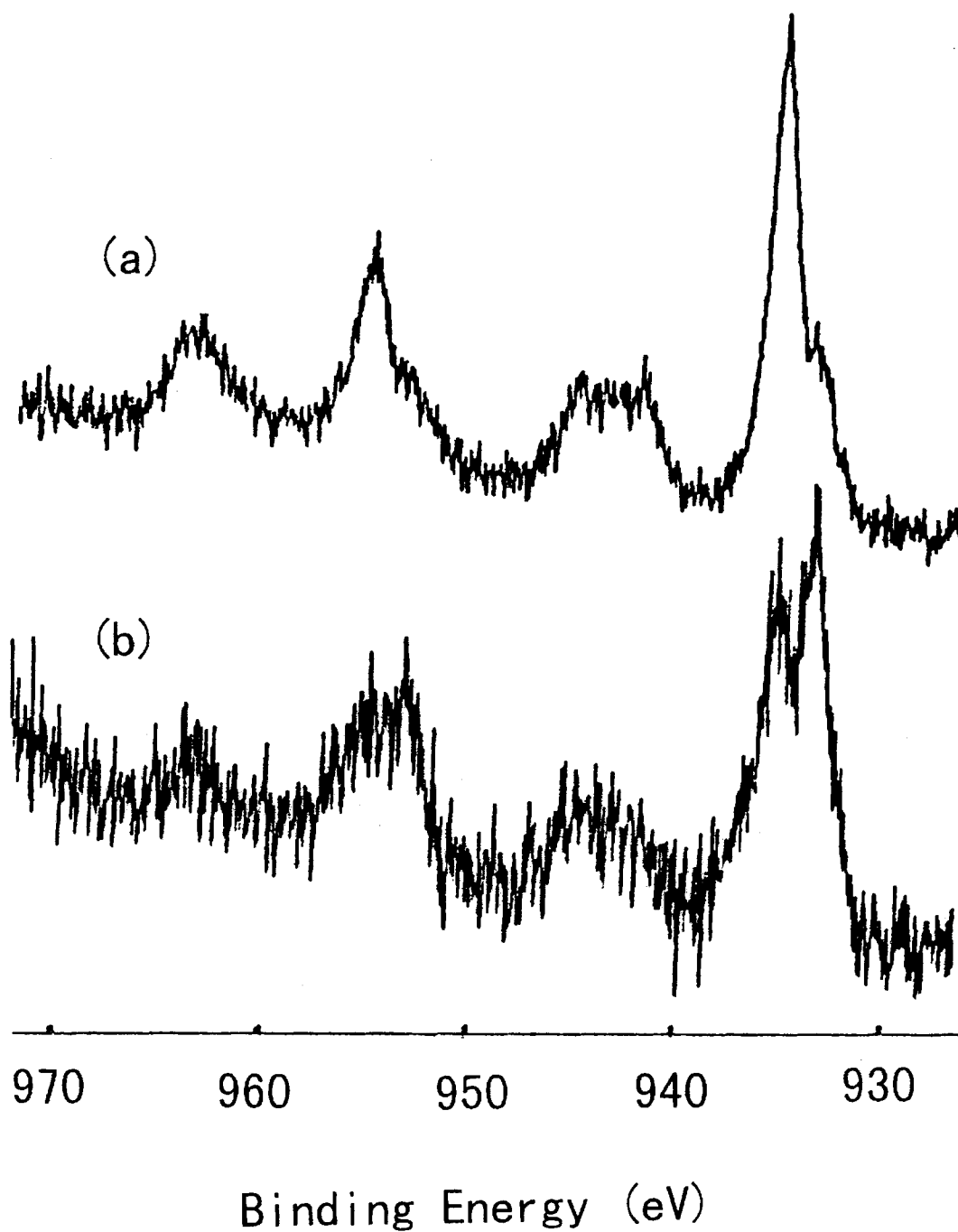


Figure 3. Cu (2p) photoelectron spectra of Pvbpy-CuCl₂.
(a) after preparation. (b) after the third reaction.

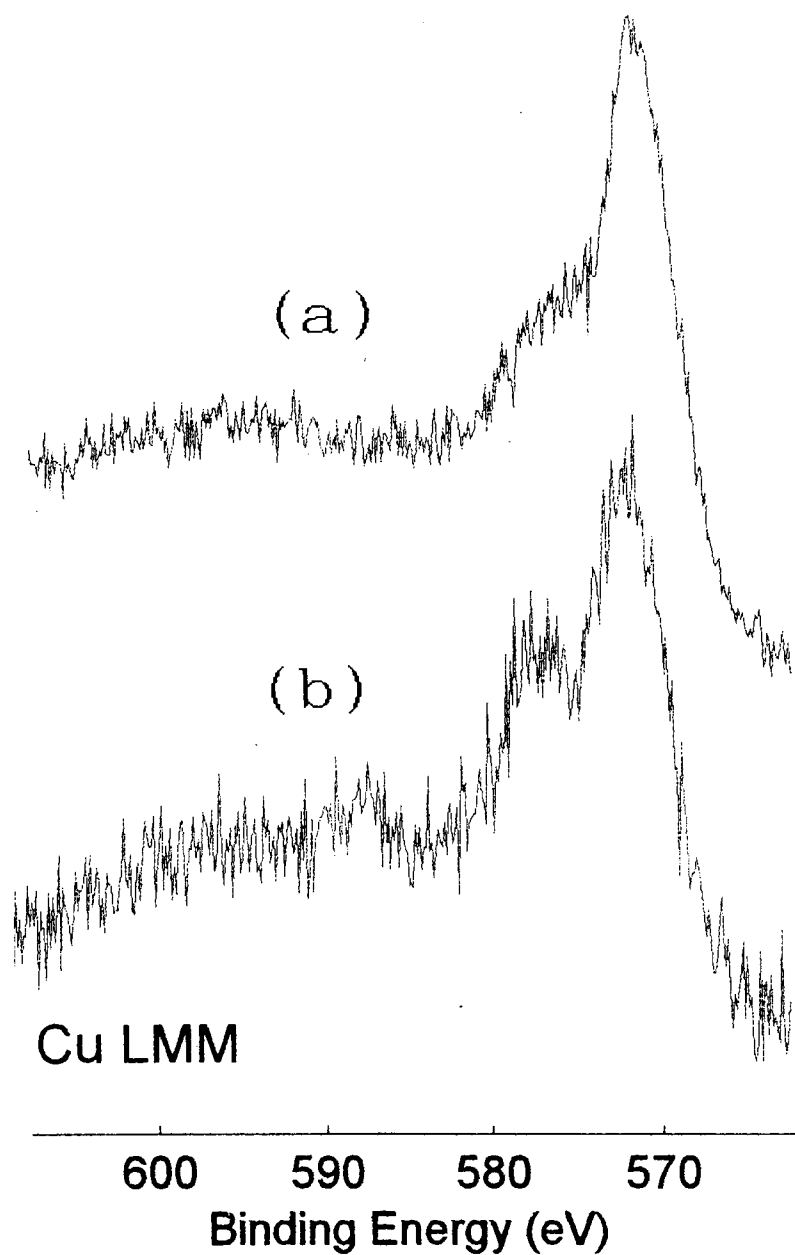


Figure 4. Cu LMM Auger transition spectra. (a) Pvbpy-CuCl₂ (fresh); (b) Pvbpy-CuCl₂ (after 3rd reaction).

two divided peak areas. About 19 % of Cu(II) was reduced to Cu(I) in the catalyst preparation procedure. During the reaction, the reduction gradually proceeded. After 6 h of reaction (3rd reaction), about 61 % of the total Cu existed as Cu(I) in the Pvbpy-CuCl₂ catalyst. Figure 4 shows the Cu LMM Auger transition of the Pvbpy-CuCl₂ catalyst. Fresh Pvbpy-CuCl₂ shows binding energy (B.E.) of ~571 eV (Figure 4 (a)), and no energy shift was observed during the reaction (Figure 4 (b)). It is reported [13] that both CuCl and CuCl₂ have kinetic energy (K.E.) of around 915~916 eV, and that Cu metal has K.E. of 918.5 eV (Figure 5) [K.E. + B.E. = 1486.6 eV (B.E. of AlK α)]. Thus, it is obvious that the transformation of Cu(II) to Cu(I) is predominant in the reaction system.

Figure 6 shows the N(1s) XPS spectra of (a) Pvbpy and (b) Pvbpy-CuCl₂ (after preparation). Pvbpy N(1s) spectra showed a peak at 398.8 eV (Figure 6 (a)), and this was shifted to higher binding energy (at 399.8 eV) by the coordination of Cu(II) (Figure 6 (b)). This higher-peak shift can be explained by the reduction of the electron density of the nitrogen atom [14] with coordination of Cu(II) because the electron of the nitrogen atom transferred to Cu(II).

It is reasonable to consider that some of the coordinated Cl⁻ is exchanged with another ligand during the reaction as well as during preparation of the catalyst. Recently, Tomishige and co-workers reported [15] on the activated carbon supported CuCl₂ catalyst. Similar results have been observed for the activated carbon-supported CuCl₂ catalyst. Leaching of Cl⁻ to a larger extent (until Cl/Cu = 0.7) was also observed during the initial step of the catalytic reaction (~90 min). In addition, the XRD study suggested that CuCl₂ was partly reduced to CuCl or received ligand-replacement reactions (e.g., to form CuCl(OH) by a reaction with H₂O). The ligand exchange of Cl⁻ was reported to occur not only during the reaction but also during preparation of the catalyst. Both active species, CuCl(OCH₃) and the other chemical species, may exist in the polymer-supported catalysts.

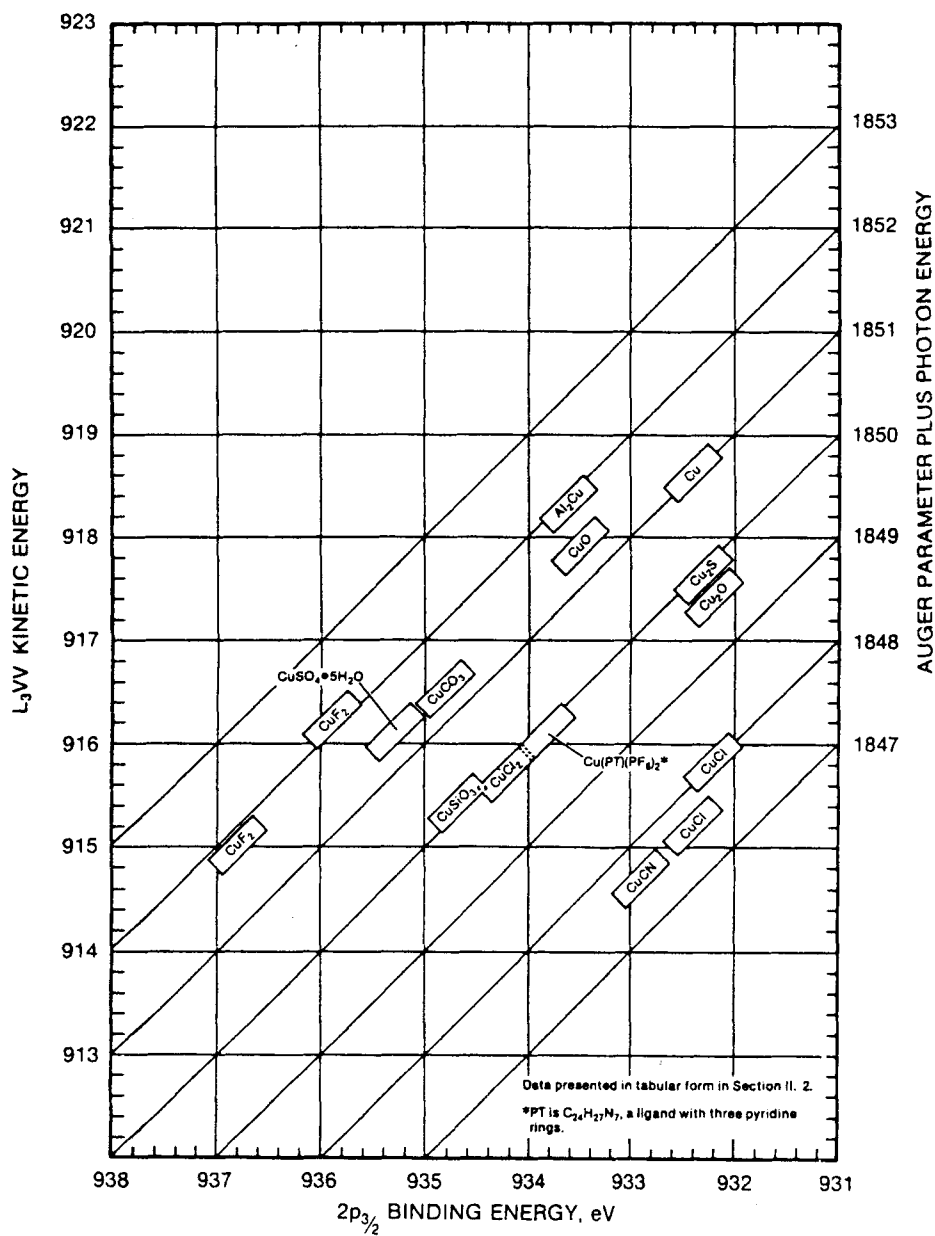


Figure 5. The relation between Cu 2p 3/2 binding energy and Cu LMM kinetic energy for various Cu complexes.
 An extract from "*Handbook of X-ray Photoelectron Spectroscopy* (Editor: G. E. Muilenberg, Published by Perkin-Elmer Co.)".

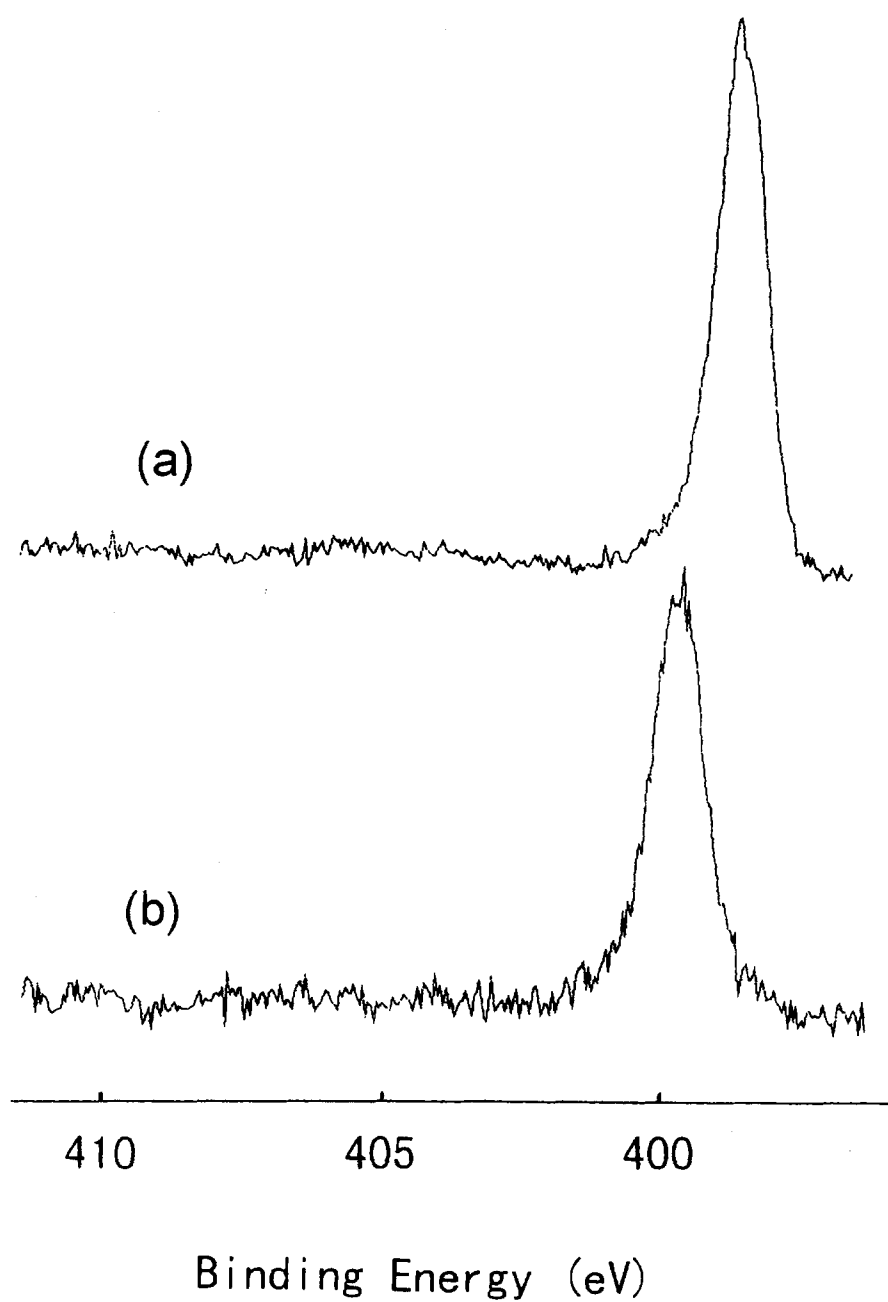


Figure 6. N(1s) photoelectron spectra. (a) Pvbpy;
(b) Pvbpy-CuCl₂ (after preparation).

The relation between the patterns of decline in the amounts of Cu and Cl in Figure 2, however, could not be fully explained by the experimental data above. we also consider that some Cl^- released was trapped as HCl by the ligand-free N atom of pyridine ring, and a certain amount of Cl in the catalyst was maintained.

4. SUMMARY

The new heterogenized catalyst, Pvbpy- CuCl_2 , was studied for synthesis of DMC by oxidative carbonylation of methanol. This catalyst showed activity almost equal to that of PVP- CuCl_2 . The Pvbpy- CuCl_2 catalyst could be recycled thrice, maintaining its initial reactivity. The Pvbpy- CuCl_2 catalyst showed good anti-corrosion property to stainless steels. The corrosiveness was closely related to the amount of Cl^- released from the Pvbpy support, which was the main cause of corrosion in the reaction system. From the XPS study of the catalyst, it become obvious that Cu(II) was gradually reduced to Cu(I) during the reaction.

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Chapter 3

DMC Synthesis using CuCl_2 Catalyst Supported by 8-Quinolinol

ABSTRACT

Novel immobilized CuCl_2 catalysts (Cu(ox)_2 , Cu(ox)Cl (oxH = 8-quinolinol), and PVO-Cu; PVO is a co-polymer of 2-vinyl-8-quinolinol with styrene) which includes 8-quinolinol as a coordination site, were investigated for the dimethyl carbonate (DMC) synthesis by oxidative carbonylation of methanol in liquid phase reaction. These three types of immobilized catalysts include Cl with the various ratio per Cu, and the catalytic activities (DMC yield and selectivity) were found to be closely related to the Cl/Cu mol ratio in the catalysts. Cu(ox)_2 which includes no Cl, showed no reaction activity in the DMC synthesis. Therefore Cl^- is necessary to proceed the reaction in the catalytic systems. This is in accordance with the reaction mechanism previously proposed for the DMC synthesis using CuCl catalyst, in which Cl^- plays an important role to proceed the reaction in the redox cycle of Cu(II)/Cu(I) to produce DMC. The catalytic activities of Cu(ox)Cl and PVO-Cu became lower than the homogeneous CuCl_2 catalyst. This is due to the lower Cl/Cu mol ratio of the catalysts (0.98 for Cu(ox)Cl , 0.42 for PVO-Cu) compared to CuCl_2 , in addition to the ordinary demerit of immobilization. The observed by-product is only CO_2 , therefore, DMC selectivity is representing the productivity of DMC relative to CO_2 . The relation of catalytic activities to the Cl/Cu mol ratio was studied for the above catalysts, and it was observed that DMC selectivity became higher according to the increase of Cl/Cu.

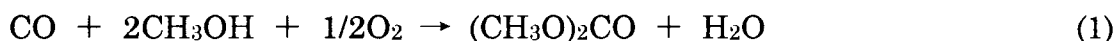
1. INTRODUCTION

Dimethyl carbonate (DMC) is a promising compound as a starting material for polycarbonate synthesis, and new processes for the polymer synthesis has been developed using DMC instead of toxic COCl_2 . DMC is also useful as methylating reagent, an additive to gasoline, and for other purposes. A synthetic process of DMC is known as an oxidative carbonylation of methanol (Scheme 1) by using copper chloride catalytic system in liquid phase, and it is industrially used [1].

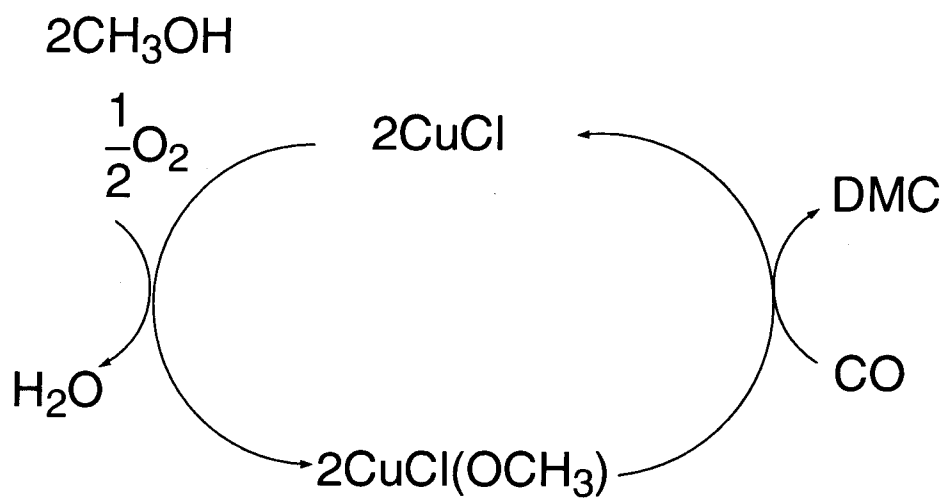
However the corrosive character of Cl^- becomes a barrier for the high productivity, because the process needs the glass lining which is expensive and low safety. Some efforts have been done to immobilize the copper chloride [2–8]. Among them, poly(4-vinylpyridine) is known as a good organic support [7, 8].

8-Quinolinol has a chelating site, and which is known to form the complexes with many metals and has been used as “trace metal precipitating reagent” from old days [9]. 8-Quinolinol is contained in coal liquid [10], therefore the effective utilization of the compound will be desirable. For that purpose, chemical modification of 8-quinolinol, for example, introducing substituents to the aromatic ring, has become very important and the polymers which include 8-quinolinol have been synthesized and investigated as the ligands to some metals [11, 12].

Catalytic systems including copper chloride are reported to be effective for the DMC synthesis by oxidative carbonylation of methanol (Eq. (1)).

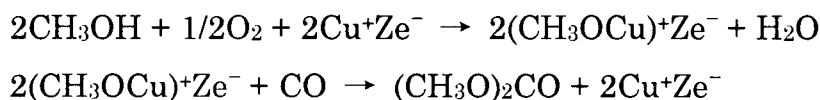


It has been considered that the Cl^- plays an important role to proceed the reaction in the redox cycle of copper in the reaction mechanism [13] (Scheme 1).



Scheme 1. Reaction mechanism proposed for CuCl catalytic system.

Recently, King reported the high productivity of DMC by using Cu catalyst supported on zeolite (Ze), which was prepared at high temperature by anhydrous ion exchange method. In this case Cl^- was not contained, and another reaction mechanism, in which Cl^- was not concerned, was proposed [14].



In this chapter, the preparation of novel immobilized CuCl_2 catalysts using 8-quinolinol as a coordination site and the application to DMC synthesis were studied. The effect of Cl^- to the productivity of DMC became clear in the DMC synthesis, using the 8-quinolinol-Cu catalysts.

2. EXPERIMENTAL

All reagents were used as received. The elemental analysis of Cu and Cl were performed by atomic absorption spectrometry and titrimetric method, respectively.

$\text{Cu}(\text{ox})_2$ and $\text{Cu}(\text{ox})\text{Cl}$ were synthesized as follows [15]. To the solution of 8-quinolinol in methanol, 1.5 equivalent of CuCl_2 as methanol solution was gradually added. Then $\text{Cu}(\text{ox})_2$ was obtained quantitatively as a dark brown powder. Calcd. for $\text{Cu}(\text{C}_9\text{H}_6\text{NO})\text{Cl}$: Cu, 26.1; Cl, 14.6 % Found Cu, 26.5; Cl, 14.5 %. IR (KBr): Ar-O⁻ vibration; Reported to be 1114 cm^{-1} Found to be 1113 cm^{-1} .

To the solution of 8-quinolinol in 50 % aqueous dioxane, 0.1 N NaOH solution was added up to pH 12. Then CuCl_2 in 50 % dioxane was added and

Cu(ox)Cl was obtained quantitatively as a yellow powder. Calcd. for Cu(C₉H₆NO)₂: Cu, 18.1; Cl, 0 % Found Cu, 18.3; Cl, 0 %. IR (KBr): Ar-O⁻ vibration; Reported to be 1118 cm⁻¹, Found to be 1118 cm⁻¹.

The polymer ligand, PVO, was obtained as follows [12, 16].

The monomer 2-vinyl-8-quinolinol was synthesized by the Wittig reaction from 2-formyl-8-quinolinol [16]. Under N₂ atmosphere, dry benzene (600 g) in a 1 L flask was stirred, and 1.6 mol/L n-butyl lithium (in hexane) (15 ml) was added to the benzene using a syringe. Wittig reagent (6.31 g: 17 mmol) was gradually added to the mixture during a period of 10 min; the color of the solution became yellow to orange. The solution was stirred for 4 h at room temperature. 2-Aldehyde-8-quinolinol (2.60 g: 15 mmol) in dry benzene was added to the solution during a period of 20 min at cooled in a water bath; the color of the reaction mixture (slurry) became red to brown. This was stirred for 1 h at room temperature, followed by for 10 min at 40 °C; the slurry part was totally dissolved. Aqueous HCl was added to the benzene solution until pH = 7, and the solvent was removed by an evaporator. The products were isolated by column chromatography on silica gel (hexane/ethyl acetate = 4/1) (total yield, 25 %).

The polymer was synthesized by radical co-polymerization of 2-vinyl-8-quinolinol with styrene in benzene at 60 °C [12] (75 % yield). Then, it was re-precipitated from methanol (obtained as a white powder). The co-polymerization ratio was calculated to be 2-vinyl-8-quinolinol : styrene = 1 : 0.86 from the elemental analysis of nitrogen. Calcd.: C, 82.4; H, 6.14; N, 5.38 % Found: C, 81.3; H, 5.90; N, 5.38 %. From GPC (THF solution) Mn/Mw was estimated to be 8700/22000.

This Cu complex, PVO-Cu was obtained as follows. The polymer was dispersed in methanol and 1.5 equivalent of CuCl₂ (per the 8-quinolinol unit) in methanol was gradually added with vigorous stirring. The polymer become soluble in methanol and dark brown solution was obtained. To the solution 0.1 N NaOH solution was gradually added until pH 7, and dark

green solid was precipitated.

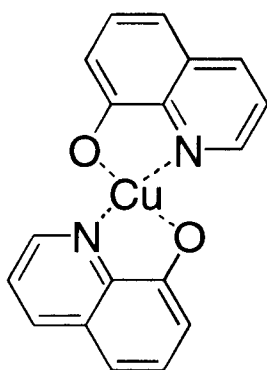
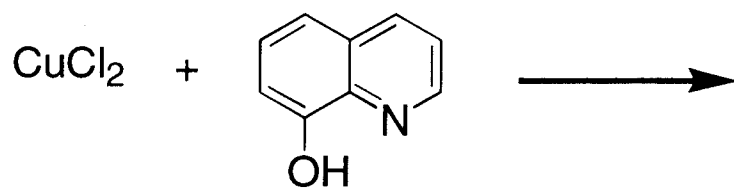
The DMC synthesis was performed in the following procedure. In a 30 ml Hastelloy C (HC)276 (Cr: 16 %, Mo: 16 %, Fe: 5 %, C: 0.01 %, Ni: base made by Mitsubishi Material Co Ltd.) autoclave, 10 ml (7.75 g) of methanol as both substrate and solvent was introduced and the catalyst was added as a powder (Cu concentration was adjusted to be 150 mM), and CO 23 kgf/cm², O₂ 2 kgf/cm² was introduced to the vapor phase. After 2 h reaction at 140 °C, the concentrations of DMC, methanol, CO₂, and O₂ were analyzed by gas chromatography. Cu(ox)₂, Cu(ox)Cl, and PVO-Cu were insoluble to methanol at room temperature, and after the reaction, the catalysts above 95 wt% was recovered by filtration and washed with methanol, thus most of Cu and Cl in the catalysts were thought to be fixed during the procedure.

3. RESULTS AND DISCUSSION

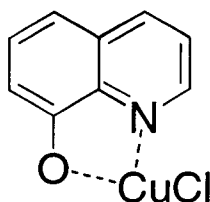
Cu(ox)₂, Cu(ox)Cl [15] (Scheme 2) and the novel polymer complex, PVO-Cu, were used as catalysts for DMC synthesis.

PVO-Cu immobilized catalyst was prepared by the reaction of CuCl₂ and PVO (Scheme 3). In the preparation of PVO-Cu, IR absorption of 3400 cm⁻¹ due to -OH group, which was observed for 2-vinyl-8-quinolinol, was disappeared and the main peaks (1564, 1505, 1453, 1383, 1329, 1109, 835, 749, 700 cm⁻¹) were identical to the reported data for the Cu complex which was prepared by the reaction of PVO and Cu(ClO₄)₂ [12], containing no Cl. It is obvious that all the 8-quinolinol units in the copolymer coordinate to Cu. Thus, all the coordination sites of PVO-Cu were assumed to consist of the mixture of Cu(ox)₂ and Cu(ox)Cl.

The ratio of Cu(ox)₂/Cu(ox)Cl in PVO-Cu was estimated as follows

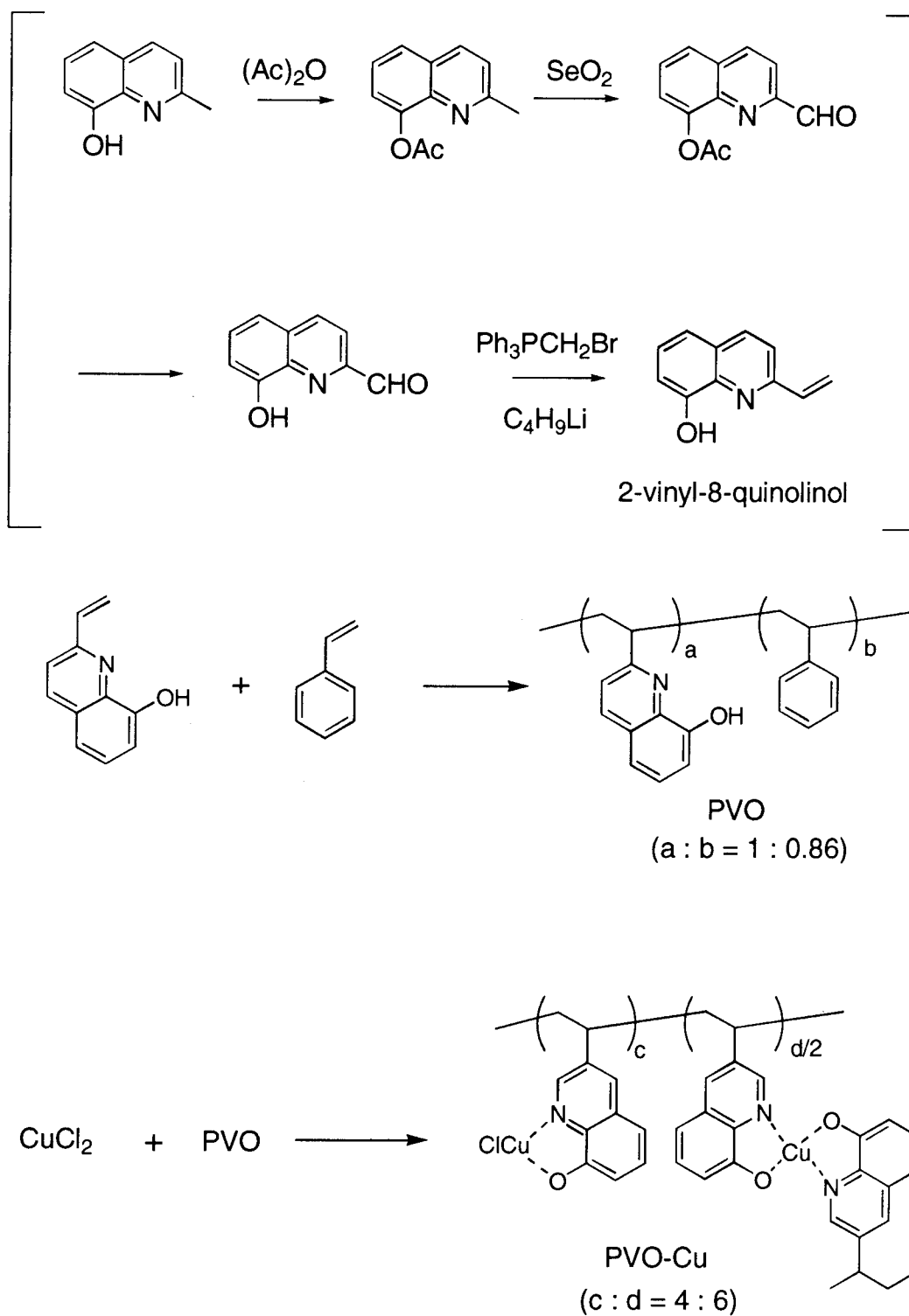


Cu(ox)_2



Cu(ox)Cl

Scheme 2. Synthesis of Cu(ox)_2 and Cu(ox)Cl (oxH = 8-quinolinol).



Scheme 3. Synthesis of PVO and PVO-Cu.

(Table 1). From the XRF measurement, Cu (%) and Cl (%) in the PVO-Cu complex were obtained to be 11.4 and 2.70 respectively. If all the 8-quinolinol unit of PVO-Cu is existing as the structure of Cu(ox)_2 , the calculated Cu (%) and Cl (%) are 10.9 and 0. Similarly, Cu (%) and Cl (%) are calculated to be 17.7 and 9.9, in the case of Cu(ox)Cl . The obtained Cu (%) and Cl (%) (11.4 and 2.70) were found in between the above two calculated values, and the ratio of $\text{Cu(ox)}_2/\text{Cu(ox)Cl}$ is estimated to be about 6/4.

Cl/Cu mol ratio of each catalyst were calculated from the Cu (%) and Cl (%), and were obtained to be 2.00 for CuCl_2 , 0.98 for Cu(ox)Cl , 0.42 for PVO-Cu, 0 for Cu(ox)_2 .

The catalytic activity of Cu(ox)Cl , Cu(ox)_2 , and PVO-Cu in the DMC synthesis has been compared, and the results are shown in Table 2. The reaction was performed in the HC276 autoclave for 2 h at 140 °C under the pressure of CO and O_2 . In this reaction condition, no by-product was detected except CO_2 by gas chromatography.

The catalytic activity (methanol conversion) of homogeneous catalysts decreased by immobilization, and the DMC yield and selectivity which were obtained in heterogeneous Cu(ox)Cl and PVO-Cu, became lower than those of homogeneous CuCl_2 . MeOH conversion and DMC yield of PVO-Cu were almost same as those of Cu(ox)Cl . On the other hand, DMC selectivity of PVO-Cu became obviously lower than that of Cu(ox)Cl . In the case of Cu(ox)_2 which contains no Cl, no DMC and CO_2 was produced.

From these results, it is obvious that MeOH conversion, DMC yield and selectivity decrease with the decrease of Cl/Cu (Figure 1), and that Cl^- is indispensable to promote the reaction. The necessity of Cl^- is well understood to form the reaction intermediate $\text{CuCl(OCH}_3\text{)}$ in the synthesis of DMC (Scheme 1).

These three immobilized catalysts were insoluble in methanol, and above 95 wt% of the used catalysts were recovered by filtration after the reaction. The demerit of immobilization caused the decrease of productivity

Table 1Cu (%)^a, Cl (%)^a, and Cl/Cu (mol ratio) in the catalysts.

Catalyst	Cu (%)	Cl (%)	Cl/Cu
Cu(ox) ₂	18.3 (18.1) ^b	0 (0) ^b	0 (0) ^b
Cu(ox)Cl	26.5 (26.1) ^b	14.5 (14.6) ^b	0.98 (1) ^b
PVO-Cu	11.4	2.7	0.42

^a From the XRF study (see Experimental).^b The calculated values for chemical fomura are represented in ().**Table 2**Catalytic activity of Cu(ox)Cl, Cu(ox)₂, and PVO-Cu relative to homogeneous CuCl₂^a.

Catalyst	Cl/Cu ^b	MeOH conv.	DMC yield	DMC sel.
CuCl ₂	2	2.76	70.0	97.4
Cu(ox)Cl	0.98	0.33	8.2	77.4
Cu(ox) ₂	0	0	0	-
PVO-Cu	0.42	0.44	10.5	59.9

^a [Cu] = 150 mM, MeOH = 10 ml, CO = 23 kgf/cm², O₂ = 2 kgf/cm²,

Temp. = 140°C, Reaction time = 2 h.

^b Cl/Cu mol ratio in the catalyst obtained from XRF.

MeOH conv. (%) = produced DMC/(introduced MeOH/2).

DMC yield (%) = produced DMC/(introduced O₂x2).DMC sel. (%) = DMC/(DMC + CO₂).

of DMC in this series of the catalysts, due to the strong binding constant of 8-quinolinol to Cu by its chelation [17]. The decomposition of Cu(ox)_2 and Cu(ox)Cl were reported to occur at 269 °C and 301 °C respectively [15], then these two catalysts are considered to be stable at the reaction temperature of 140 °C. Assuming that PVO-Cu is formed from the units of Cu(ox)_2 and Cu(ox)Cl , PVO-Cu is also considered to be stable at the reaction condition, and was confirmed to be stable (no decrease of weight was observed) up to 140 °C at atmospheric pressure of air.

For the usual continuous flow synthesis of DMC in vapor phase using the supported CuCl_2 catalyst, methanol conversion is maintained around 5 % [14]. However, the present research is carried out under a lower O_2 concentration (methanol conversion is about 2 %) to avoid dangerous sudden explosion.

Generally, the effect of corrosion resistance is observed by the immobilization of homogeneous catalyst, in which halide anion is included as a source for corrosion. HC276 (Ni base stainless steel) was used as material of autoclave, and almost no corrosion was observed for the three immobilized catalysts in appearance. On the other hand, vigorous corrosion was observed for homogeneous CuCl_2 .

Consequently, in the reaction system, Cl^- is necessary to produce DMC, and DMC selectivity which is closely related to the productivity of CO_2 is directly influenced by the amount of Cl. The necessity of Cl^- is in accordance with the reaction mechanism proposed for CuCl catalytic system [13] (Scheme 1), in which Cl^- participates in the redox cycle of copper to proceed the reaction.

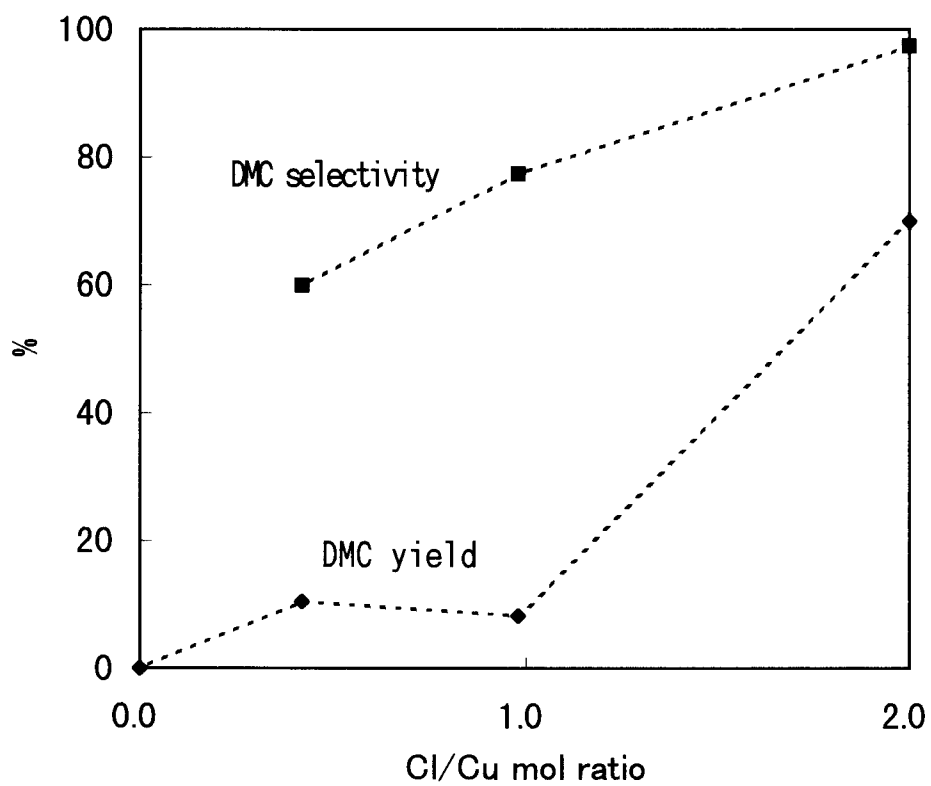


Figure 1. The trend of DMC yield and selectivity versus Cl/Cu mol ratio in the catalysts.

4. SUMMARY

Three novel immobilized catalysts which includes 8-quinolinol as a coordination site in the support were investigated for the DMC synthesis by oxidative carbonylation of methanol. Two catalysts, Cu(ox)Cl and PVO-Cu, which have Cl^- showed catalytic activity, on the other hand, Cu(ox)₂ which have no Cl^- showed no catalytic activity. In the catalytic system, Cl^- is necessary to proceed the reaction, which is in accordance with the reaction mechanism for the CuCl catalytic system. In particular, DMC selectivity, was largely influenced by the amount of Cl/Cu mol ratio in the catalyst.

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Chapter 4

Novel Effective Poly(2,2'-bipyridine-5,5'-diyl)-CuCl₂ Catalyst for the Synthesis of DMC by Oxidative Carbonylation of Methanol

ABSTRACT

A novel type of polymer-supported CuCl₂ catalyst for DMC (dimethyl carbonate) synthesis has been obtained by choosing π -conjugated poly(2,2'-bipyridine-5,5'-diyl) (PBpy) as the supporting ligand; its catalytic activity for oxidative carbonylation of methanol in the liquid phase reaction has been investigated. The catalyst gives higher DMC yield and DMC selectivity than similar heterogeneous poly(4-vinylpyridine) (PVP)-CuCl₂ catalyst. The high catalytic activity is associated with the π -conjugated conductive properties of the supporting ligand, PBpy. Both the PBpy-CuCl₂ and PVP-CuCl₂ catalysts can be easily recycled after filtration, and the catalytic activity is maintained after 3 times use. The PBpy-CuCl₂ catalyst is much less corrosive toward stainless steels compared with the PVP-CuCl₂ and ligand-free CuCl₂ catalyst.

1. INTRODUCTION

Poly(2,2'-bipyridine-5,5'-diyl) (PBpy) has been recently synthesized as one of the π -conjugated conductive polymers [1]. Metals can be easily captured by PBpy by forming chelate complexes with the bipyridyl unit. It is reported that PBpy and its Pt complex show catalytic activity for photoevolution of H_2 from aqueous media [2]. In this catalytic reaction, the soft and unique redox properties of conductive polymer which originate from the expanded π -conjugation system are considered to play an important role. Additionally, Cu(II)/Cu(I)/Cu(0) reversible redox cycles are observed in the cyclic voltammogram of a Cu complex of alkyl-substituted-PBpy; the Cu complex shows an metal-to-ligand charge transfer (MLCT) absorption-visible spectrum, suggesting possibilities of various types of electron transfer in the complex [3]. For these reasons, PBpy is expected to be useful for a support of $CuCl_2$ in the DMC synthesis, which involves Cu(II)/(I) redox cycle [24]. However, PBpy has so far not been used for such a purpose.

Dimethyl carbonate (DMC) is a promising compound as a starting material for polycarbonate. Processes using DMC, instead of toxic $COCl_2$, for the polymer synthesis has been developed. DMC is also useful as an additive to gasoline, as a methylating reagent, and for other purposes. However, DMC has mostly been produced from $COCl_2$, and development of alternative synthetic processes without using $COCl_2$ has been desired.

$CuCl$ and $CuCl_2$ are known as effective catalysts for the production of DMC by oxidative carbonylation of methanol. Industrially, DMC has been manufactured by using $CuCl$ as a catalyst [4]. However, the manufacturing system becomes a slurry liquid due to poor solubility of $CuCl$ in methanol, and the catalyst shows strong corrosive effect toward metallic vessels due to coexistence of halide anion and the active hydrogen compound [5].

In order to avoid the corrosion, glass lining of the vessel is carried out. However, this is very expensive, and corrosive explosion initiated by the

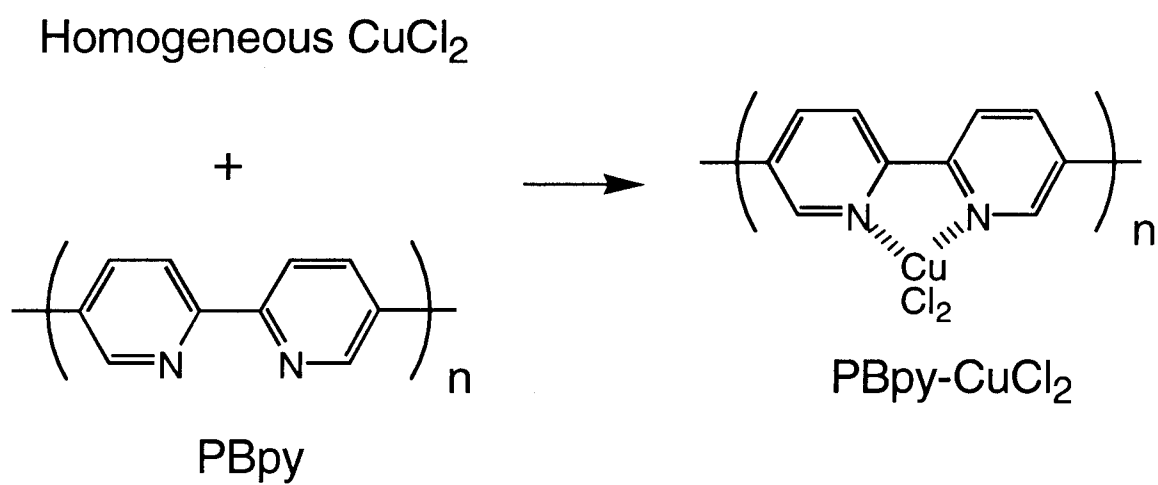
cracking of the glass has been worried about. Because of these reasons, scaling up the manufacturing system, which is important for improvement of the productivity of DMC, has been restricted. CuCl_2 , which is soluble in methanol, is also effective as a homogeneous catalyst to produce DMC, and high reactivity and selectivity have been found for the DMC synthesis. Unfortunately, the catalytic system is also corrosive toward the reaction vessel [6].

Many researchers have tried to immobilize copper chlorides on support [7–11]. Usefulness of the immobilized catalysts has been mostly tested for vapor phase reactions, and the catalytic system has been found almost free from corrosion. Active carbon serves as an excellent support for copper chlorides; however, the catalyst gradually loses the chloride anion and its catalytic activity in a continuous flow process [7]. Because of this reason, development of new effective catalysts by using appropriate supports has been desired. Y type zeolite binds Cu more tightly by an ion exchange and the stability of the supported catalyst has been reported to be high enough [8]. Recently, it has also been reported that solid-state ion-exchanged Cu(I) Y zeolite is active for the oxidative carbonylation of methanol [9].

Poly(4-vinylpyridine) (PVP) is known as a good support for CuCl_2 in the liquid phase reaction of DMC synthesis. However, due to its low melting point, elevation of the reaction temperature is difficult [22]. A cross-linked PVP can avoid this problem to some extent [23].

On the other hand, a chelating π -conjugated polymer, PBpy, has recently been synthesized as one of the conducting polymers [1]. This polymer forms various metal complexes, and the metal complexes show unique electronic and optical properties due to its having the expanded π -conjugation system. [12–14].

We have found that PBpy is a very useful support of CuCl_2 for the DMC synthesis (Scheme 1). The CuCl_2 complex of PBpy has high thermal and chemical stability and serves as an effective catalyst, which may originate



Scheme 1. Immobilization of CuCl_2 by PBpy.

from the unique electronic state of PBpy. The chelating effect of PBpy is considered to contribute to make the complex highly stable. Such a metal complex of π -conjugated polymer ligand has not been used as a catalyst for the DMC synthesis.

2. EXPERIMENTAL

2.1. Preparation of the PBpy-CuCl₂ Complex

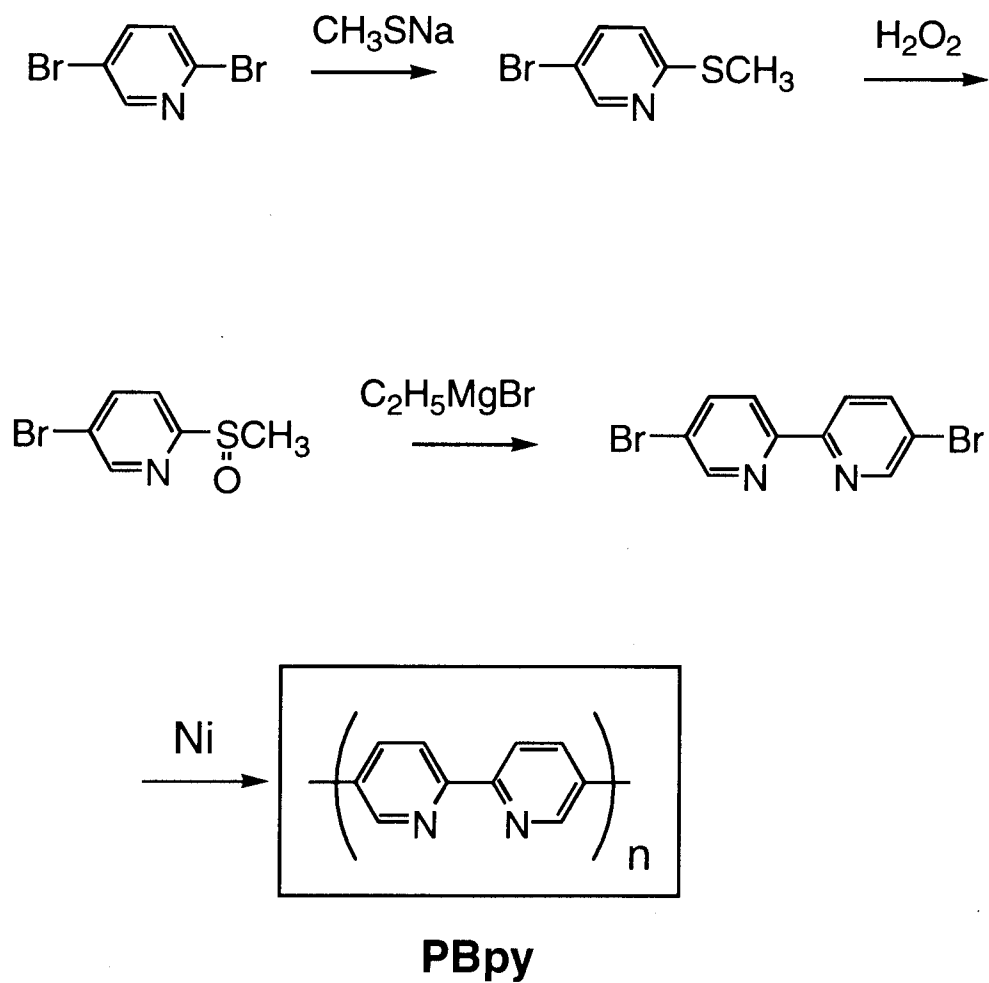
PBpy was synthesized according to the literature [1]. 5,5'-Dibromo-2,2'-bipyridine was polymerized by using a Ni(0) complex as a debromination reagent (Scheme 2).

Synthesis of 5-Bromo-2-Methylsulfenylpyridine

2,5-Dibromopyridine (676 g: 2.85 mol), aqueous 15 % CH₃SNa (2000 g: 4.29 mol), tetra n-butylammoniumbromide (25.3 g), and benzene (1000 ml) were introduced into a 5 L reactor, and the mixture was refluxed overnight. After extraction by toluene from the mixture, the combined organic layer was washed with water and dried over MgSO₄, and the solvent was evaporated. 5-Bromo-2-methylsulfenylpyridine (yield, 89.5 %; 520 g) was distilled to obtain bp 83~86 °C/4 mmHg.

Synthesis of 5-Bromo-2-Methylsulfinylpyridine

To 5-bromo-2-methylsulfenylpyridine (515 g: 2.53 mol) and CH₃CO₂H (1400 ml) in a 3 L reactor, 30 % H₂O₂ (344 g) was gradually added. The mixture was cooled in an ice bath and stirred overnight. The reaction mixture was neutralized by 28 % aq. NH₃, and extracted with CH₂Cl₂. The



Scheme 2. Synthesis of PBpy support.

organic layer was washed by water and dried over MgSO_4 , and the solvent was evaporated. 5-bromo-2-methylsulfinylpyridine (yield, 86.8 %; 483 g) was purified by silica gel column chromatography (ethyl acetate/hexane = 2/1).

Synthesis of 5,5'-Dibromo-2,2'-Bipyridine

Into 5-bromo-2-methylsulfinylpyridine (250 g: 1.14 mol) and THF (5.1 L) in a 10 L reactor, 1.0 M $\text{C}_2\text{H}_5\text{MgBr}$ (THF solution) (760 ml) was gradually added for 40 min at $< 20^\circ\text{C}$. The mixture was stirred for 3 h at room temperature and poured into 50 L of water. The precipitate was filtered off and washed first with water and then with 1 L of acetone (3 times) and dried. 5,5'-dibromo-2,2'-bipyridine (yield, 25.2 %; 90 g; GLC purity $> 99\%$) was obtained by recrystallization from DMF.

Synthesis of Poly(2,2'-Bipyridine-5,5'-diyl) (PBpy)

5,5'-Dibromo-2,2'-bipyridine (78.0 g: 0.25 mol), 2,2'-bipyridine (46.8 g: 0.3 mol), 1,5-cyclooctadiene (107.7 ml), $\text{Ni}(\text{cod})_2$ (85.8 g: 0.312 mol), and anhydrous DMF (1620 ml) were added into a 3 L reactor under Ar atmospheric condition, and the mixture was stirred for 66 h at 70°C . The obtained precipitate was washed with hot toluene, warm EDTA aq. (pH = 3), warm EDTA aq. (pH = 9), warm NaOH aq. (pH = 9), and hot toluene, in that order. Poly(2,2'-bipyridine-5,5'-diyl) (yield, 66.5 %; 25.5 g) was obtained. The polymer contained 8.8 % of Br, although the previously reported PBpy contained only a negligible amount of Br [1]. If both terminals of the polymer contain Br, the degree of the polymerization ('n' in Scheme 2) is estimated at about 9~10. Found: C, 68.9; H, 4.03; N, 15.95; Br, 8.8 %. Calcd. for $\text{Br}(\text{C}_{10}\text{H}_6\text{N}_2 \cdot 0.2 \text{H}_2\text{O})_{10}\text{Br}$: C, 69.1; H, 3.71; N, 16.12; Br, 9.2%. The ^1H -NMR (solvent: deuterated formic acid DCO_2D) and IR data are identical to those given in the literature.

PBpy (light yellow powder) and the 2 equiv. of CuCl_2 were allowed to

react in methanol for 5 h under reflux. The PBpy-CuCl₂ catalyst was obtained as a green-yellow powder which was not soluble in methanol. X-ray fluorescence spectrometry (XRF) revealed that the obtained complex contained 16.9 wt% of Cu and 18.8 wt% of Cl. These results indicated that about 72 mole% (in the case $n = 10$) of the 2,2'-bipyridyl (bpy) units of PBpy was coordinated to CuCl₂.

After the reaction (after 3 times recycled use), XRF revealed that the PBpy-CuCl₂ catalyst contained 17.0 wt% of Cu and 16.6 wt% of Cl. These results indicated that the catalyst contained 73 mole% of Cu and 59 mole% of Cl₂ per the bpy units of the PBpy support. These results suggested that Cu was not lost from the supporting polymeric ligand and that a part of the Cl ligand was replaced by some other ligand like OCH₃.

The used PVP was non-crosslinked and contained 10 % styrene unit as a co-polymerization component; the powder was purchased from Aldrich Co. Ltd. The powder was soluble in methanol at room temperature, and had a melting point of around 110 °C. The PVP-CuCl₂ catalyst was prepared in a manner similar to that applied for the preparation of PBpy-CuCl₂, and obtained as a green powder. This complex was insoluble in methanol. The ratio of CuCl₂/pyridine was estimated to be about 1/2 from the elemental analyses of Cu and Cl.

2.2. DMC Synthesis

Into a 30 ml Hastelloy C (HC) 276 (Cr: 16 %, Mo: 16 %, Fe: 5 %, C: 0.01 %, Ni: base; made by Mitsubishi Material Co Ltd.) autoclave, 10 ml of methanol and 528 mg of the PBpy-CuCl₂ catalyst were added ([Cu] = 150 mM). Then CO (23 kgf/cm²) and O₂ (2 kgf/cm²) were introduced into the autoclave. After 2 h stirring at 140 °C, amounts of DMC, methanol, CO₂, and O₂ were estimated by gas chromatography.

The rate of corrosion was separately evaluated from the following experiments. SUS316 (Cr: 18 %, Mo: 2 %, Ni: 10 %, C: 0.08 %, Fe: base) and HC276 were used as test pieces (dimensions: about 15 mm×6 mm×2 mm; weight (density): for SUS316, 2.0 ± 0.2 g (7.92 g/cm^3), for HC276, 3.0 ± 0.3 g (8.87 g/cm^3)), and added into the reactor. These test pieces were insulated from the inside wall of the reactor by using a Teflon (Du Pont) seal. The rate of corrosion [mg h^{-1}] represents the decrease of the weight of the test pieces. This evaluation method had an experimental error of about 0.1 mg h^{-1} .

3. RESULTS AND DISCUSSION

3.1. *Catalytic Activity of PBpy-CuCl₂*

The activity and selectivity of the several types of catalysts for the DMC synthesis has been compared; the results are shown in Table 1. In this reaction condition, no by-product except CO₂ was detected by gas chromatography.

For the usual vapor phase continuous flow synthesis of DMC using the supported CuCl₂ catalyst, methanol conversion is maintained around 5 % [9]. The present research is carried out under a lower O₂ concentration (methanol conversion is about 2 %) to avoid any dangerous sudden explosions.

Usually the catalytic activity of homogeneous catalysts becomes lower by immobilization. PVP belongs to the most widely used supports for the immobilization of some homogeneous catalysts [15–21]. Due to the above mentioned reason, the DMC yield and selectivity obtained with the PVP-CuCl₂ catalyst are lower than those of homogeneous CuCl₂ (Table 1).

However, the DMC yield and selectivity obtained with the PBpy-CuCl₂ are higher than those of PVP-CuCl₂ and are comparable to those of homogeneous CuCl₂.

When equimolar amounts of 2,2'-bipyridine (Bpy) with CuCl₂ were added to the reactor as a catalyst (Bpy-CuCl₂ catalyst in Table 1), immediately, a part of Bpy-CuCl₂ complex was precipitated before the reaction. However, the high catalytic activity (DMC yield and DMC selectivity) which is comparable to the activity of homogeneous CuCl₂ was achieved (Table 1). When the solution was cooled to room temperature after the reaction, the Bpy-CuCl₂ complex was gradually precipitated from the solution. Additionally, severe corrosion to HC276 was observed, likely to the case of homogeneous CuCl₂ catalyst. Thus, it could be considered that the Bpy-CuCl₂ catalyst is almost homogeneous at the reaction condition (140 °C, ~30 kgf/cm²).

The PBpy-CuCl₂ catalyst is also considered to suffer from the general demerit of the immobilization. In spite of the demerit, the PBpy-CuCl₂ catalyst attains the high DMC yield and selectivity. PBpy can mediate electron transfer through the polymer chain [2], which accelerates the catalytic reaction. The expanded π -conjugation system of PBpy will enable the occurrence of unique redox reactions of the supported metals [1] and seems to afford excellent results.

In addition, PBpy has high thermal stability and is stable even at 250 °C. This suggests that the PBpy-CuCl₂ catalyst is usable at high temperature with high activity. A high heat resistance is one of the important characters for the catalyst to give high activity. On the other hand, the melting point of the non-crosslinked PVP is much lower (around 110 °C). According to its low melting point, the catalytic reaction by using the PVP-CuCl₂ catalyst has been carried out at lower temperature [22]. An improved cross-linked PVP-CuCl₂ catalyst is usable up to 140 °C [23].

The PBpy-CuCl₂ and PVP-CuCl₂ catalysts were able to be recycled after

simple filtration and washing with methanol. About 5 wt% loss of the PBpy-CuCl₂ catalyst was observed for each recycling. In the repeated catalytic runs, fresh catalyst was added to maintain the Cu concentration of 150 mM. In the case of the PVP-CuCl₂ catalyst, the weight loss is larger (about 10 wt%). This larger loss observed with the PVP-CuCl₂ seems attributable to good solubility of PVP in methanol. On release of CuCl₂ from insoluble PVP-CuCl₂ catalyst, PVP will be dissolved in methanol, and only 90 wt% of the original catalyst was recovered by the filtration and washing. The IR spectrum of a sample obtained after drying up the soluble part supports the good solubility of PVP in methanol, by showing a peak at 1597 cm⁻¹ which is assigned to ν (C=N) of the pyridine ring coordinated to Cu²⁺ (ν (C=N) of free PVP is 1615 cm⁻¹). This disadvantage of PVP can be overcome by making it insoluble in methanol by introduction of cross-linking to the polymer by the copolymerization with divinylbenzene.

Table 2 compares results of the catalytic reactions using the PBpy-CuCl₂ and PVP-CuCl₂ catalysts. Both the catalysts maintain their catalytic activities for 3 uses. The DMC yield and DMC selectivity of the PBpy-CuCl₂ catalyst are higher than those of the PVP-CuCl₂ catalyst.

PBpy 261 mg (1.5 mmol) and Cu(I)Cl 149 mg (1.5 mmol) were simultaneously introduced in the autoclave as the PBpy-CuCl catalyst, and the above DMC synthetic reaction was performed. After the 1st reaction, the insoluble part was filtered, washed with methanol, and used for the next reaction as the recycled catalyst (2nd). It was confirmed that Cu species were coordinated to the PBpy support, because the main IR peaks were totally identical to the PBpy-CuCl₂ catalyst.

Comparing the catalytic activity of the PBpy-CuCl₂ catalyst, the obtained DMC yield and selectivity for the PBpy-CuCl catalyst became lower level (Table 3). It is not clear from only these experimental results that the coordination state (ligand for Cu, Cu coordinating ratio for N site, etc.) is in the same level for comparing the both catalytic activities, or not.

Table 1

Catalytic activity of the PBpy-CuCl₂ catalyst compared with those of the PVP-CuCl₂ and homogeneous CuCl₂ catalyst^a.

Catalyst	MeOH conv.	DMC yield	DMC sel.
PBpy-CuCl ₂	2.72	68.1	94.2
PVP-CuCl ₂	1.84	47.1	91.4
CuCl ₂	2.76	70.0	97.4
Bpy-CuCl ₂	2.92	70.4	95.8

^a [Cu] = 150 mM, MeOH = 10 ml, CO = 23 kgf/cm², O₂ = 2 kgf/cm²,

Temp. = 140°C, Reaction time = 2 h.

MeOH conv. (%) = produced DMC/(introduced MeOH/2).

DMC yield (%) = produced DMC/(introduced O₂x2).

DMC sel. (%) = DMC/(DMC + CO₂).

Table 2

Catalytic activity of the PBpy-CuCl₂ and PVP-CuCl₂ catalysts in recycled use^a.

Catalyst	MeOH conv. ^b	DMC yield ^b	DMC sel. ^b
PBpy-CuCl ₂ 1st use	2.72	68.1	94.2
PBpy-CuCl ₂ 2nd use	2.91	73.0	97.1
PBpy-CuCl ₂ 3rd use	2.76	70.0	97.4
PVP-CuCl ₂ 1st use	1.84	47.1	91.4
PVP-CuCl ₂ 2nd use	2.04	52.8	92.2
PVP-CuCl ₂ 3rd use	2.16	55.9	91.0

^a The concentration of Cu was maintained at 150 mM by adding the catalyst in the 2nd and 3rd runs (cf. the text). The catalytic reaction was carried out under the same conditions given in the caption of Table 1.

^b As in Table 1.

The optimum Cl/Cu ratio for the catalytic system is considered to be higher than 1.

3.2. Rate of Corrosion

Rates of corrosion of the steels caused by the PBpy-CuCl₂ and PVP-CuCl₂ catalysts are listed in Table 4 (after 1st use and after recycled (3rd use), together with the data obtained with homogeneous CuCl₂. The test period is short (2~4 h), and the experiment has an estimated experimental error of about 0.1 mg h⁻¹. The data shown in Table 1 clearly indicate that homogeneous CuCl₂ has a much higher corrosive effect to both SUS316 and HC276 than the PBpy-CuCl₂ and PVP-CuCl₂ catalysts. On the other hand, the PBpy-CuCl₂ and PVP-CuCl₂ catalysts show only a minor corroding effect.

It has been reported that the severe corroding effect of halogen ions can be largely improved by immobilization [20–23]. PVP has been used not only to support the homogeneous catalysts [15–21] but also to retard the corrosion in the DMC synthesis from methanol [22, 23]. The data shown in Table 4 agree with the reported effect of the PVP support to decrease the corrosive effect of Cl⁻.

As described in the above section, the PBpy-CuCl₂ catalyst shows excellent catalytic activity for the DMC synthesis, and the corrosive effect of CuCl₂ was remarkably reduced. As seen in Table 4, this anti-corrosive effect of the PBpy support is larger than the PVP support. For the PBpy-CuCl₂ and PVP-CuCl₂ catalysts, their corrosive effect become very weak at the recycled use. However, in their first use, the PVP-CuCl₂ catalyst was more corrosive than the PBpy-CuCl₂ catalyst. For the PVP-CuCl₂ catalyst, a part of CuCl₂ may be only weakly supported and be responsible to the corrosion of steels at the 1st cycle.

Table 3

Catalytic activity of the Pbpy-CuCl catalyst, in the 1st use and recycled (2nd), compared to that of the PBpy-CuCl₂ catalyst^a.

Catalyst	MeOH conv.	DMC yield	DMC sel.
PBpy-CuCl ₂ (1st)	2.72	68.1	94.2
PBpy-CuCl(1st)	0.88	22.1	74.3
PBpy-CuCl(2nd)	0.88	22.2	77.0

^aThe reaction conditions is in the footnote of Table 1.

Table 4

Rates of corrosion of steels caused by the PBpy-CuCl₂ and PVP-CuCl₂ catalysts and homogeneous CuCl₂^a.

Catalyst		Rate of corrosion /mg h ⁻¹	
		SUS316 ^b	HC276 ^b
PBpy-CuCl ₂	1st use	0.2	<0.1 ^c
PBpy-CuCl ₂	recycled (3rd use)	<0.1 ^c	<0.1 ^c
PVP-CuCl ₂	1st use	2.3	0.9
PVP-CuCl ₂	recycled (3rd use)	0.2	<0.1 ^c
homogeneous CuCl ₂		39.6	8.3

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

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

^c Within the limit of detection.

Pitting corrosion, which can not be clearly estimated from the loss of weight, in spite of its crucial importance for practical use [5], was observed for both the PVP-CuCl₂ and PBpy-CuCl₂ catalysts (Figure 1). SUS316 received the pitting corrosion with higher number density than HC276. The present results suggest that SUS316 and HC276 themselves are not usable as the material for the reactor and the glass lining is inevitable.

However the explosive danger caused by cracking of glass lining layer may be avoided by using HC276, since the corrosive effect of the PBpy-CuCl₂ catalyst is very weak. Future research for industrial application is necessary by improvement of the PBpy-CuCl₂ catalyst (e.g., by changing the molecular weight of the polymer and the composition of the catalyst).

The freshly prepared PBpy-CuCl₂ catalyst contains 72 mole% of Cu and 72 mole% of Cl₂ (or 144 mole% of Cl) per the bpy (2,2'-bipyridyl) unit of the PBpy support. The content of Cu was maintained even after the 3rd use. However, the content of Cl₂ decreased after the use. The content of Cl₂ decreased to 59 mole% (or 118 mole% of Cl) (Figure 2).

It has been reported that the true active species for the DMC synthesis by CuCl catalyst can be assigned to CuCl(OCH₃) and that the other chemical species may be also formed in the reaction system [24]. The Cl ligand of CuCl₂ are considered to be gradually replaced by other ligands like OCH₃, and this released Cl⁻ is regarded as a main corroding material.

It can be interpreted that no Cu was released from PBpy even after 3rd use; however, a part of the Cl⁻ ligand is released. As described above, for the PVP-CuCl₂ catalyst, CuCl₂ itself was released from PVP. It is noticeable that PBpy-CuCl₂ showed the highest catalytic stability, releasing almost no Cu during the 6 h reaction. The π -conjugation system of PBpy might bring about stronger binding force toward the Cu atom in the DMC synthesis.

To pursue the origin of the strong binding force between PBpy and Cu, we conducted preliminary semi-empirical and *ab initio* molecular orbital (MO) calculations. In Table 5 and Figure 3, the calculated MO energy levels

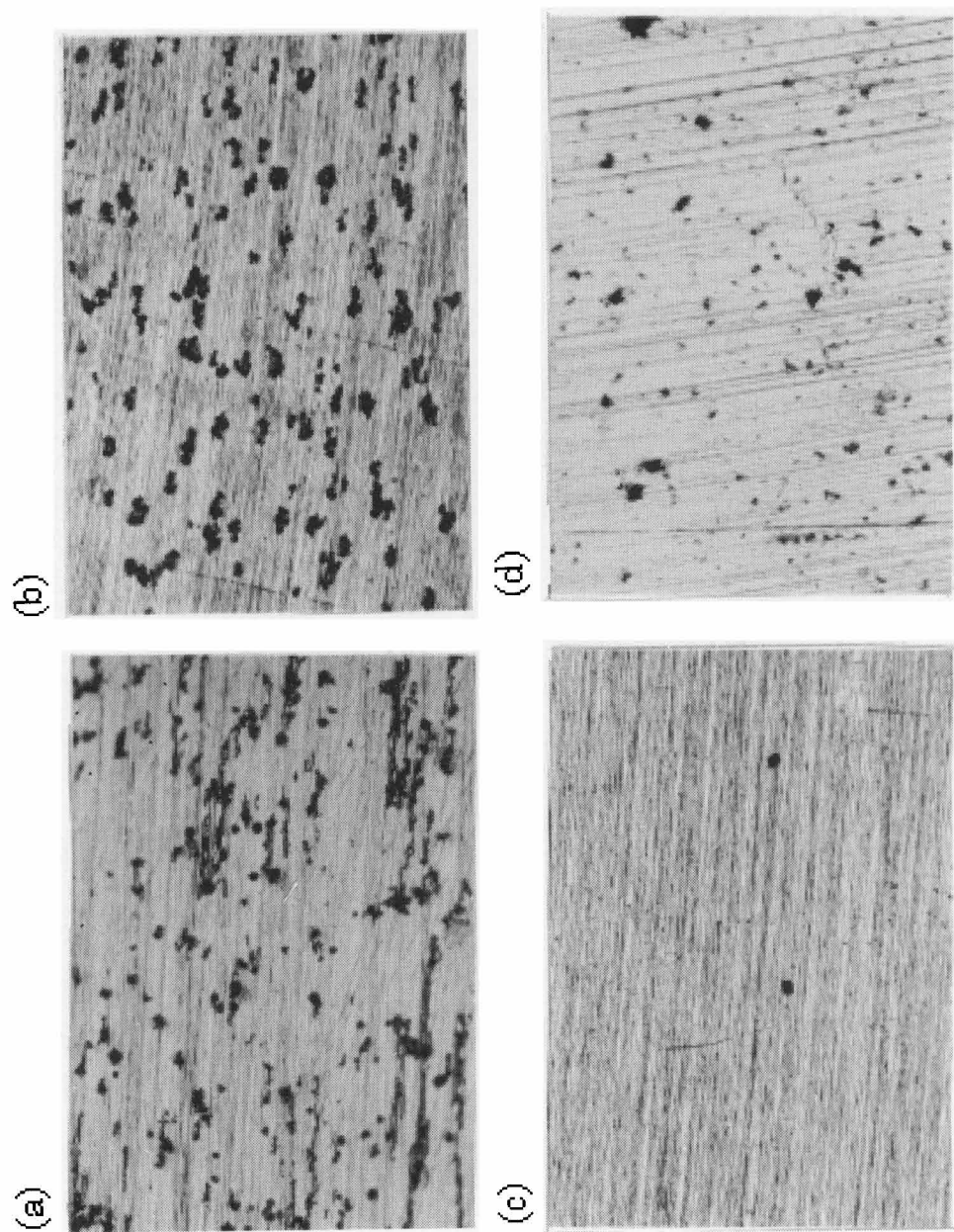


Figure 1. Pitting corrosion observed at test pieces for recycled catalysts (range: X200).

These test pieces were put into the autoclave at the reaction conditions for 4 h.

(a) PBpy-CuCl₂ (SUS316); (b) PVP-CuCl₂ (SUS316); (c) PBpy-CuCl₂ (HC276); (d) PVP-CuCl₂ (HC276).

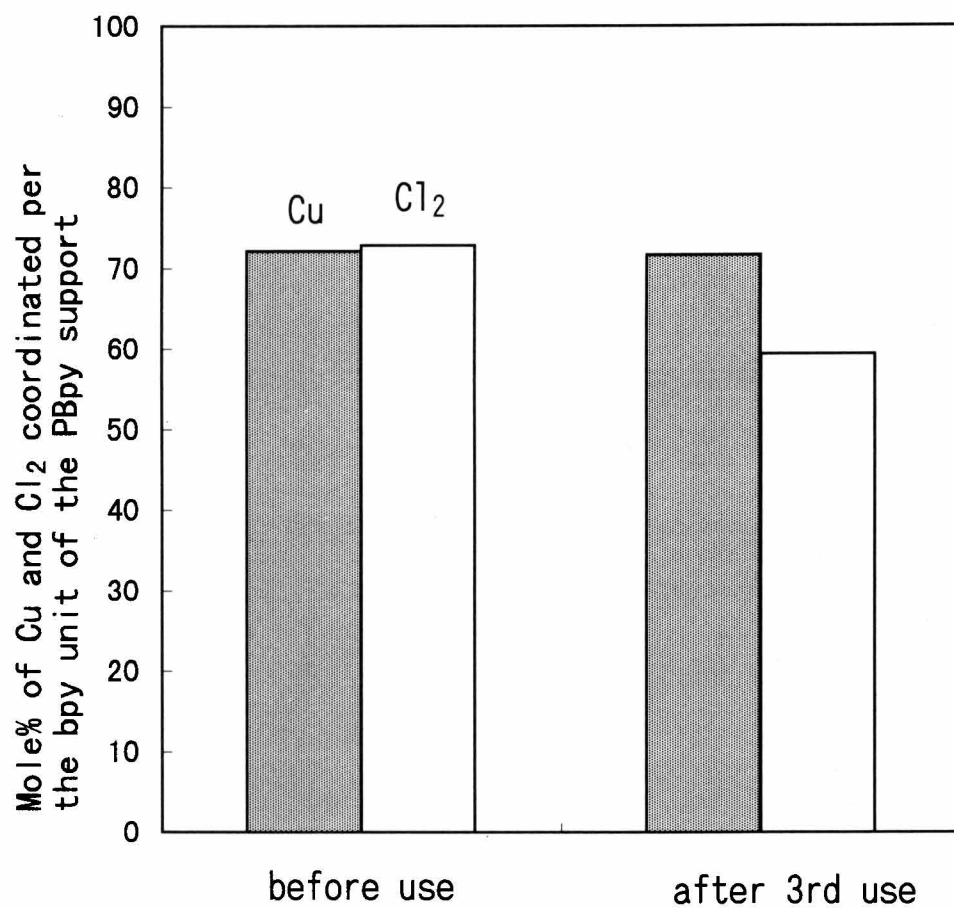


Figure 2. The coordination ratio of Cu and Cl₂ in the PBpy-CuCl₂ catalyst. Based on analysis of Cu and Cl by XRF (cf. Experimental). Reaction conditions: as in Table 1–3.

for MOPAC/PM3 and RHF/lanl2dz (method/basis) are shown and plotted versus the degree of polymerization (DP) value: n . We found that the larger the DP of PBpy is, the lower the lowest unoccupied (LU) MO energy of PBpy becomes as a result of the long π -conjugation. Further, the LUMO energy levels obviously fall to lower levels compared to those of the monomer ($n = 1$), while the HOMO ones do not change very much. Because the lower LUMO energy could promote the π -back donation from metal to the pyridine ring and lower the total energy level of the complex (Scheme 3), the origin of the strong binding force may be enhanced π -back donation from Cu(I) species [25], which are produced as intermediate in Scheme 4.

3.3. Reaction Mechanism

Formation of DMC molecule from MeOH and CO requires oxidation processes involving two electron transfer. Consequently, the redox properties of the catalyst must be closely related to its catalytic activity. Scheme 4 represents a mechanism for the Cu(II)Cl₂-catalyzed synthesis of DMC. Previously, for the Cu(I)Cl catalytic system, U. Romano and his co-workers proposed that two reaction intermediates **2** and **4** gave DMC. The catalytic cycle is considered to involve the Cu(II)/Cu(I) redox reactions such as those expressed by paths (d) and (e) [24].

Intermediate **1** undergoes the ligand exchange reaction (a) to give **2**. This is converted into **3** by addition of CO (path (b)), which receives the CO insertion to generate **4** (path (c)). The two Cu(II) species, **2** and **4**, are considered to react to afford DMC (step (d)) and two molecules of a Cu(I) complex, **5**. The starting complex **1** is generated by the oxidation of the Cu(I) species with O₂ (step (e)). In this mechanism, the electron transfer process is very important.

In the Wacker type homogeneous oxidation of ethylene catalyzed by Pd

Table 5

Calculated MO energy level for PBpy.

	MOPAC/PM3		RHF/3-21g		RHF/lanl2dz	
	N-lone-pair	N- π	N-lone-pair	N- π	N-lone-pair	N- π
n = 1	-0.3752	0.0002	-0.4004	0.1300	-0.4087	0.1045
n = 2	-0.3686	-0.0269	-0.3944	0.0972	-0.4050	0.0868
n = 4	-0.3682	-0.0479	-0.3939	0.0724	-0.4028	0.0629
n = 6	-0.3700	-0.0553	-0.3970	0.0638	-0.4035	0.0538
n = 8	-0.3693	-0.0578				
n = 10	-0.3701	-0.0600				

unit: hartree (1 hartree=627.51 kcal/mol)

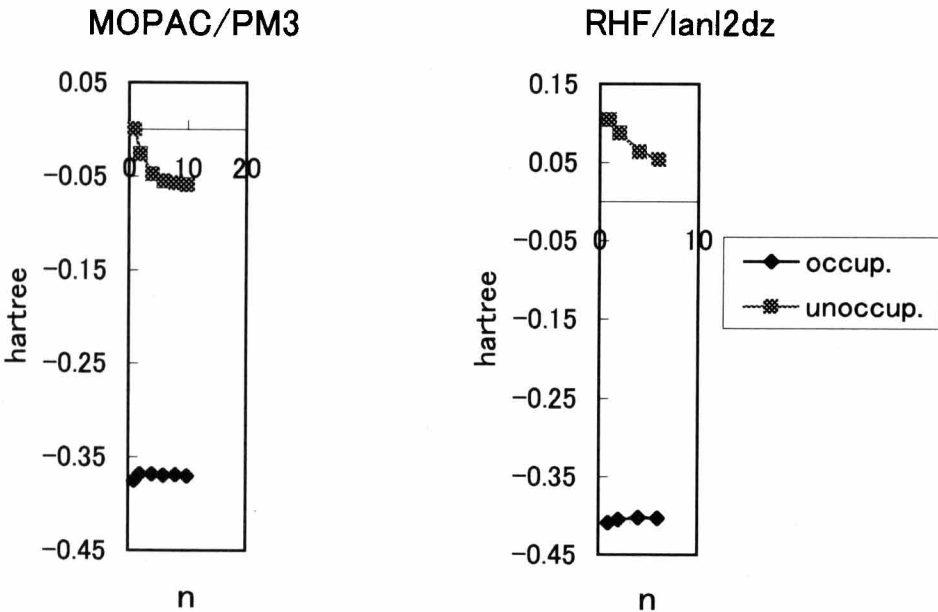
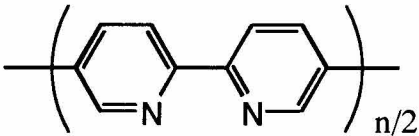
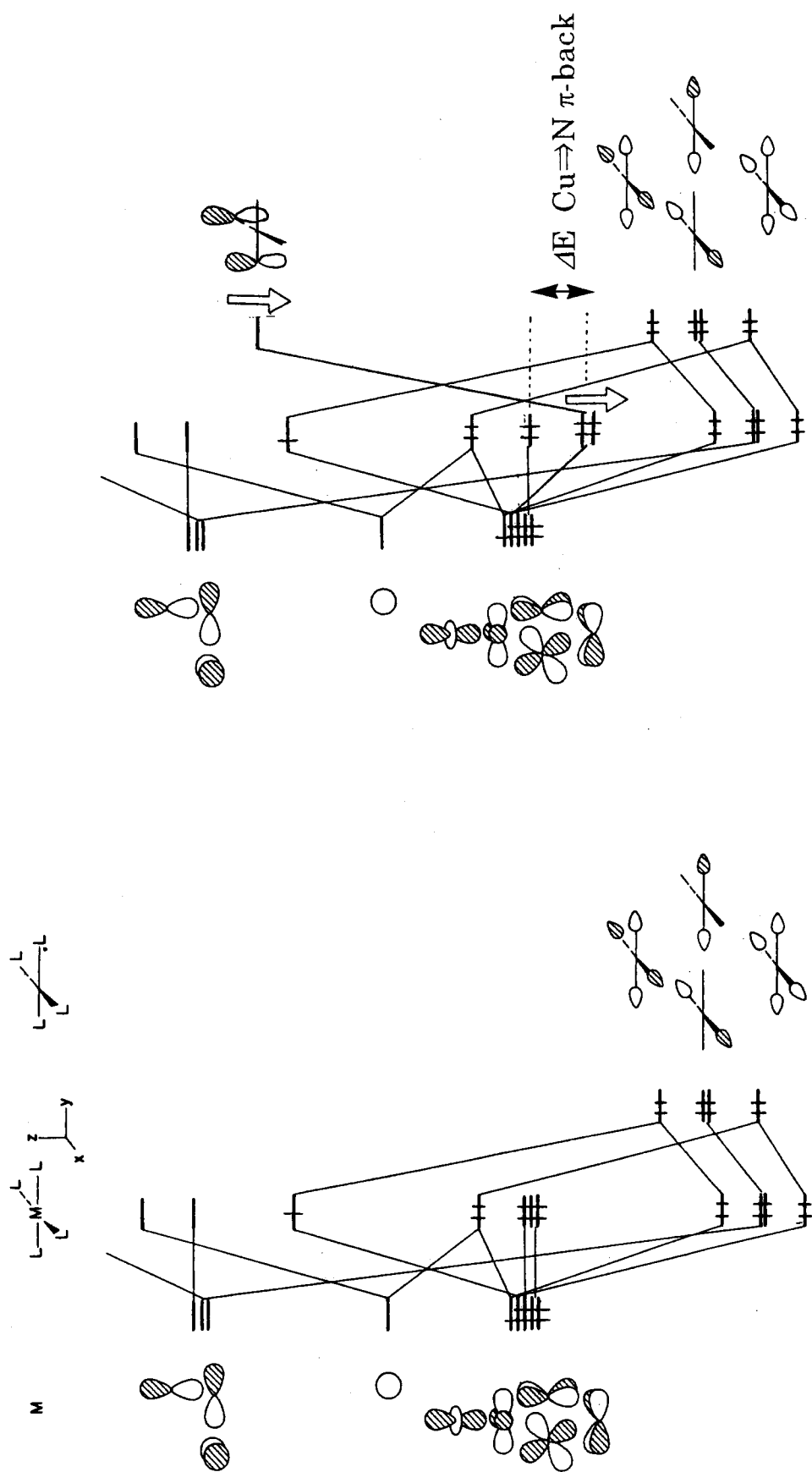


Figure 3. Calculated MO energy level for PBpy.

Energy level of N-lone-pair (occup.), N- π MO (unoccup.) are plotted for MOPAC/PM3, RHF/lanl2dz, versus n value (ref. Table 5).



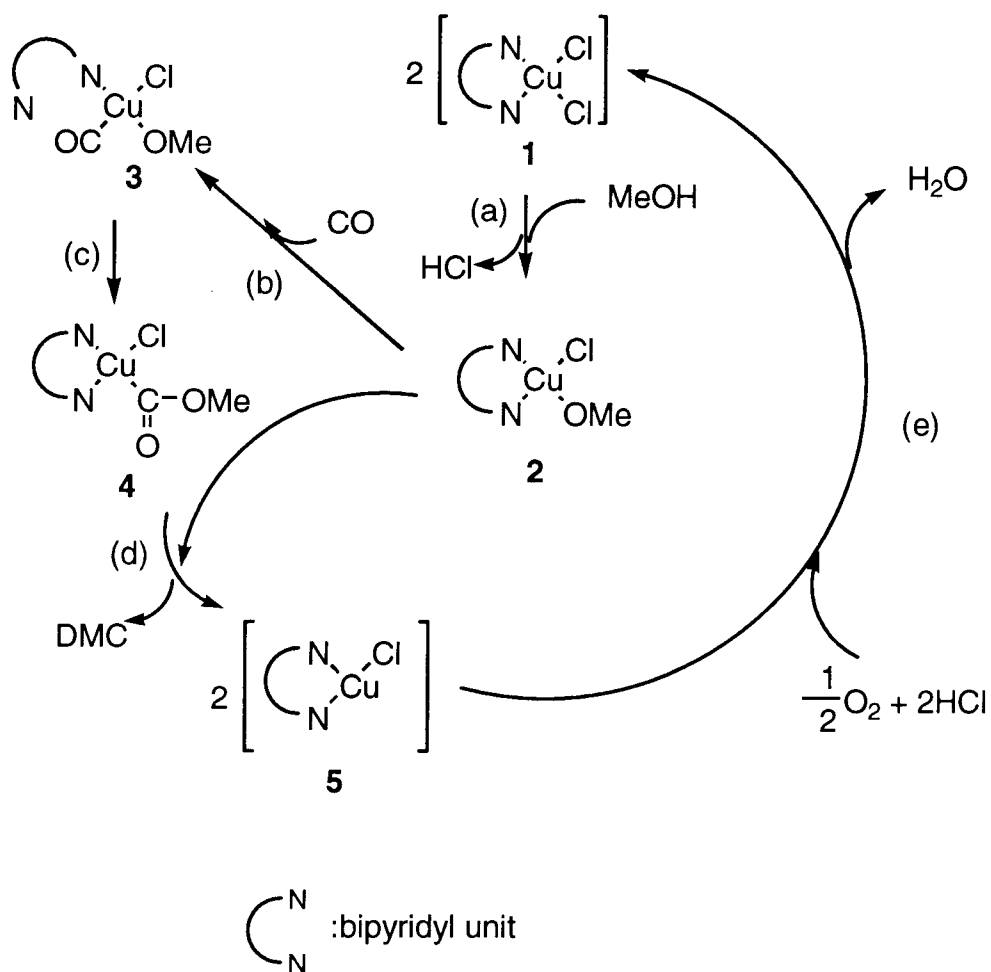
Scheme 3. Image of the total MO energy for the PBpy-CuCl₂ complex (applied for the square planar model).

Right: supposed to exist π -back donation; Left: do not supposed.

and Cu, which is considered to involve a similar redox process, a catalyst containing electronically contacted Pd and Cu through a Cl bridge shows very high activity [26]. For example, Pd and Cu randomly supported on Y zeolite show only low activity in the gas phase reaction, however, absorption of H₂O enhances the catalytic activity. Absorbed H₂O is considered to serve as a carrier of electrons to give the high catalytic activity [27].

In the homogeneous CuCl₂ catalytic system, there is much more opportunity for **2** and **4** to approach within the distance to occur “step (d)”, which enable the reduction of Cu(II) to produce DMC. On the other hand, when Cu species were immobilized on support, the opportunity might be decreased. For the PBpy-CuCl₂ and PVP-CuCl₂ catalytic systems, the above-mentioned disadvantage may be overcome by special electron transfer assisted by certain chemical species. The solvent including MeOH, DMC and H₂O, may be playing this role, because even the non π -conjugated PVP-CuCl₂ shows considerable catalytic activity.

In the case of the PBpy support, it may have an additional accelerating effect due to the presence of the expanded π -conjugated conductive system, which can transfer electrons. The higher catalytic activity of the PBpy-CuCl₂ catalyst than that of the PVP-CuCl₂ catalyst may be attributed to facile occurrence of the redox reaction of the Cu species due to easy electron transfer through the polymer chain. Similar electron transfer through an support has been proposed to explain high catalytic activity by Wacker type catalysts supported on active carbon [28, 29].



Scheme 4. Proposed reaction mechanism.

4. SUMMARY

The new PBpy-CuCl₂ catalyst has been prepared, and its catalytic activity for the DMC synthesis has been investigated. The catalyst shows higher activity than the PVP-CuCl₂ catalyst. The PBpy-CuCl₂ catalyst can be recycled without loss of its initial reactivity. The π -conjugated conductive character of the PBpy support is considered to be an important factor to accelerate the Cu(II)/(I) redox cycle. The PBpy-CuCl₂ catalyst shows better corrosive behavior toward HC276 than the PVP-CuCl₂ catalyst, which is associated with the higher stability of the PBpy-CuCl₂ complex.

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Chapter 5

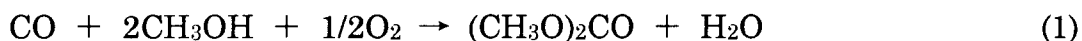
Poly(pyridine-2,5-diyl) - CuCl₂ Catalyst for the Synthesis of DMC by Oxidative Carbonylation of Methanol

ABSTRACT

A π -conjugated polymer, Poly(pyridine-2,5-diyl) (PPy) was investigated as a support for CuCl₂ in the synthesis of dimethyl carbonate by oxidative carbonylation of methanol. The PPy-CuCl₂ adduct had high catalytic activity which was comparable to that of the homogeneous CuCl₂ catalyst. The adduct caused corrosion of stainless steel vessels only to minor extent, compared with the homogeneous CuCl₂ catalyst. This PPy-CuCl₂ catalyst was easily recycled by filtration and showed a similar catalytic activity in the third time use. The presence of 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.

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, oxidative carbonylation of methanol (Eq. (1)) by 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 catalyst regeneration procedure by adding HCl into the reactor [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(4-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(4-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]. In the

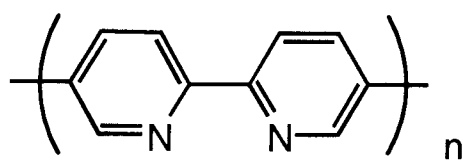
previous chapter, we prepared novel type of polymer-supported CuCl_2 catalysts for the DMC synthesis, and a CuCl_2 complex of π -conjugated poly(2,2'-bipyridine-5,5'-diyl) (PBpy) [11], had higher catalytic activity and stability than the poly(4-vinylpyridine)- CuCl_2 catalyst. The presence of π -conjugated system in the polymer is considered to facilitate redox reaction of copper involved in the catalytic reaction [12].

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

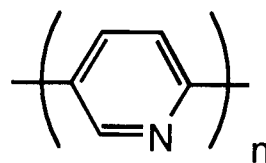
2. EXPERIMENTAL

PPy was synthesized as follows (Scheme 2). 2,5-Dibromopyridine (400 g, 1.69 mol) purchased from Tokyo Kasei Co., Ltd. was polymerized by using $\text{Ni}(\text{PPh}_3)_4$ as a debrominating reagent [11]. $\text{Ni}(\text{PPh}_3)_4$ 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 the reference [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.

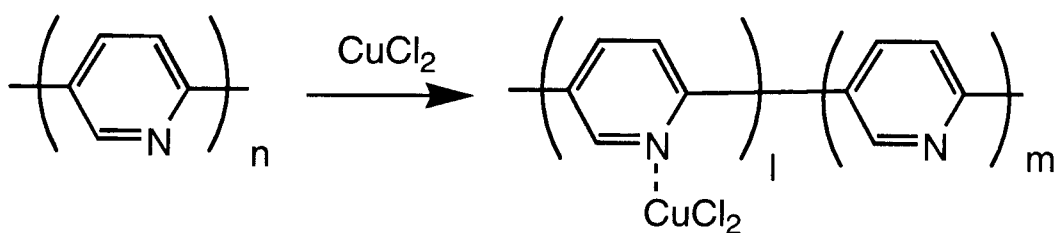
Inherent viscosity $[\eta]$ of the obtained PPy was 0.27 dl g^{-1} in HCOOH , which indicated that the polymer had a molecular weight of about 2000 or



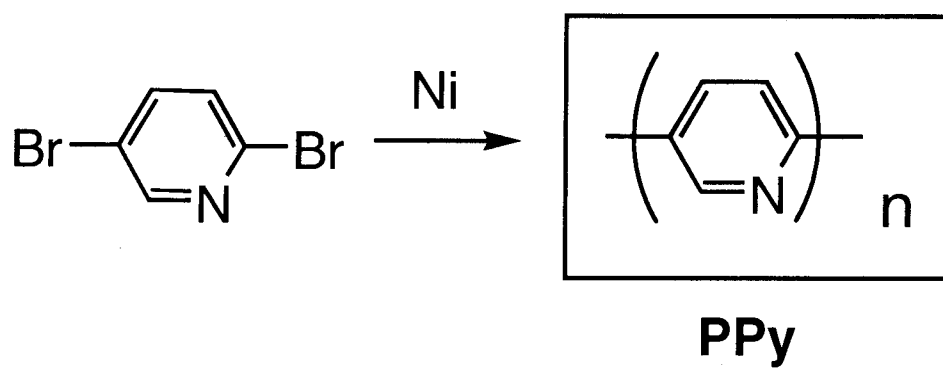
PBpy



PPy



Scheme 1. Molecular structures of PBpy and PPy.
Immobilization of CuCl_2 by PPy.



Scheme 2. Ni(0) catalyzed debromination for synthesis of PPy polymer.

lower, as judged from the $[\eta]$ value of 0.85 dl g^{-1} obtained for PPy with a molecular weight of 3800 [11]. It was reported that use of $\text{Ni(PPh}_3)_4$ 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]. A 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 3 time recycled use, 13.9 wt% of Cu and 13.8 wt% of Cl were found.

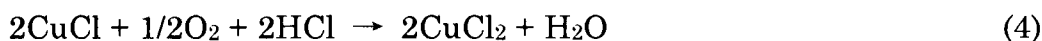
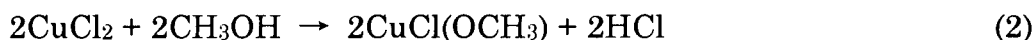
The DMC synthesis was performed according to the following procedure. In an autoclave, 10 ml (7.75 g) of methanol, which served as the substrate and solvent, and PPy- CuCl_2 powder (719 mg) were added ($[\text{Cu}] = 150 \text{ mM}$). Then, CO (23 kgf/cm^2), and O_2 (2 kgf/cm^2) were introduced in the 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 $\text{CH}_3\text{OH}/2$)), DMC yield (%) (= produced DMC/(introduced $\text{O}_2 \times 2$)), 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 $15 \text{ mm} \times 6 \text{ mm} \times 2 \text{ mm}$) of SUS316 (Cr: 18 %, Mo: 2 %, Ni: 10 %, C: 0.08 %, Fe: base; weight = $2.0 \pm 0.2 \text{ g}$) and Hastelloy C(HC)276 (Cr: 16 %, Mo: 16 %, Fe: 5 %, C: 0.01 %, Ni: base; made by Mitsubishi Material; weight = $3.0 \pm 0.3 \text{ g}$) 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-CuCl₂ catalyst (e.g., PPy-CuCl₂ (1st use) in Table 1) was compared with those of the homogeneous CuCl₂ catalyst and the PBpy-CuCl₂ catalyst at a CH₃OH conversion of about 3 %, and the results are shown in Table 1. Under the reaction conditions, no by-product other than CO₂ was detected by gas chromatography, and the DMC selectivity was calculated from the following equation: DMC/(DMC + CO₂).

In the previous chapter, we reported that PBpy gave higher catalytic activity in the CuCl₂-promoted DMC synthesis than poly(4-vinylpyridine), which is one of the most generally used support for CuCl₂ (cf. the last line in Table 1). A reaction mechanism involving Cu(II)/Cu(I) redox processes has been proposed for the DMC synthesis using the copper chloride catalyst [13]:



The presence of 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.

The molar ratio of Cu per the pyridine unit was 40 mole% before the catalytic reaction (just after the preparation) in the PPy-CuCl₂ catalyst. The amount of Cl₂ per the pyridine unit was 34 mole% (or 68 mole% of Cl) which is lower than that of Cu, indicating that all of the coordinated Cu species did not exist as CuCl₂. Similar results were reported for the activated carbon-supported CuCl₂ catalyst [14], and it was suggested that CuCl₂ was partly reduced to CuCl or received ligand replacement reactions (e.g., that to form CuCl(OH) by a reaction with H₂O).

Table 1

Catalytic activity of the PPy-CuCl₂ catalyst in comparison with those of the PBpy-CuCl₂ catalyst, the poly(vinylpyridine)-CuCl₂ catalyst, and the homogeneous CuCl₂ catalyst^a.

Catalyst ^b	CH ₃ OH 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	2.72	68.1	94.2
homogeneous CuCl ₂	2.76	70.0	97.4
poly(4-vinylpyridine)-CuCl ₂	1.84	47.1	91.4

^a [Cu] = 150 mM, CH₃OH = 10 ml, CO = 23 kgf/cm², O₂ = 2 kgf/cm²,

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 CH₃OH conv. = produced DMC/(introduced CH₃OH/2);

DMC yield = produced DMC/(introduced O₂x2);

DMC sel. = DMC/(DMC + CO₂).

As shown in Table 1, the DMC yield and DMC selectivity of the PPy-CuCl₂ catalyst were comparable to those of the PBpy-CuCl₂ catalyst and the homogeneous CuCl₂ catalyst. The high yield and selectivity are also ascribed to the presence of the π -conjugated system in PPy. The PPy-CuCl₂ catalyst could be recycled, and high yield and selectivity were found in the 3rd use (cf. The data of PPy-CuCl₂ (2nd use) and PPy-CuCl₂ (3rd use) in Table 1), although the initial catalytic activity was somewhat decreased.

Some CuCl₂ leaching from the PPy-CuCl₂ catalyst support was observed during the reaction; thus, the released CuCl₂ may exhibit some catalytic activity. The CuCl₂ leaching was also observed for the poly(4-vinylpyridine)-CuCl₂ catalyst; however, the catalyst apparently showed the lower catalytic activity than the PPy-CuCl₂ catalyst (Table 1). Therefore, the contribution of the released CuCl₂ to the DMC synthesis is considered to be insignificant level for comparing the data in Table 1.

The amount of coordinated CuCl₂ was estimated before the reaction (0 h), after the 1st reaction (2 h), and after the 3rd reaction (total reaction time = 6 h). The results are shown in Figure 1, where mole% values of CuCl₂ (Cu and Cl₂) supported by the pyridine unit of PPy are plotted versus the total reaction time.

During the 1st catalytic reaction (0 ~ 2 h), the amounts of Cu and Cl₂ per the pyridine unit were decreased to 30 and 25 mole%, respectively. During the 2nd and 3rd catalytic reactions (2 ~ 6 h), the amounts of Cu and Cl₂ were eventually decreased to 26 and 22 mole%, 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) [in Chapter 4].

Leaching of Cl⁻ to a larger extent was also observed during the initial step of the catalytic reaction using the activated carbon-supported CuCl₂ 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 [in Chapter 2]. 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. the Experimental part) 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(4-vinylpyridine)- CuCl_2 catalysts [in Chapter 4]. The corroding effect at the 1st catalytic use was larger than that at the recycled (3rd) 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 1st use.

As described above, PPy seems to be useful as a support for CuCl_2 in the DMC synthesis. However, further improvement of the catalytic system is required. It is necessary to find better reaction conditions (temperature, pressure, etc.) to prevent CuCl_2 leaching from the PPy- CuCl_2 catalyst. The higher polymerized PPy which has stronger binding force to CuCl_2 will be obtained by the modified method. Precision procedure to prepare the PPy- CuCl_2 complex will also be important.

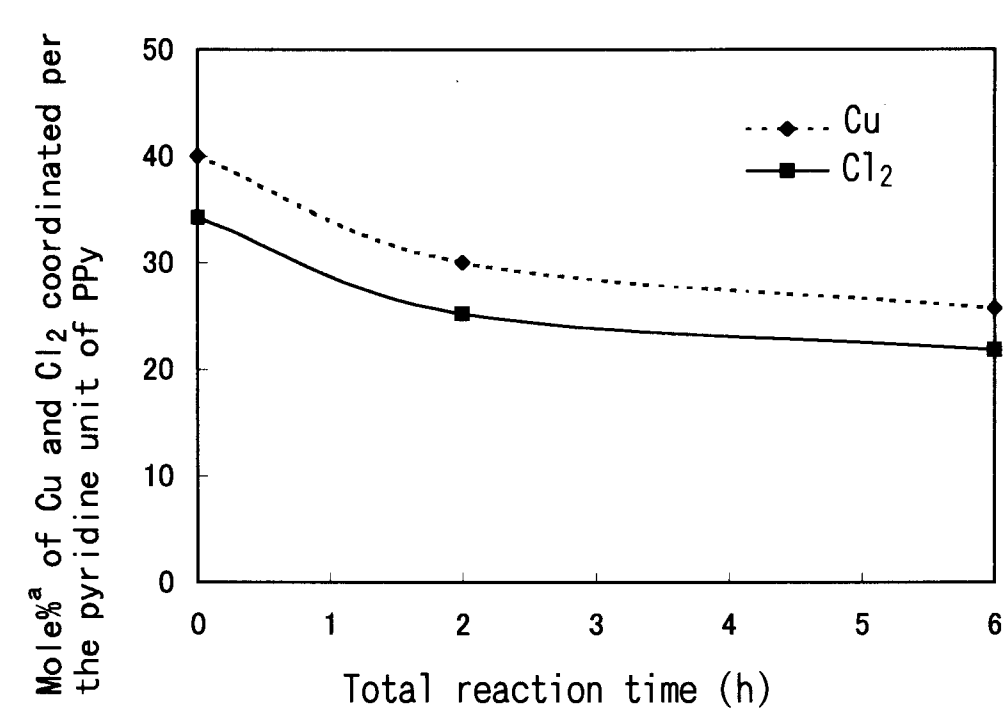
Table 2
 Rate of corrosion^a caused by the PPy-CuCl₂ catalyst in comparison with the homogeneous CuCl₂ catalyst.

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	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.



^a Mole% is calculated from Cu, Cl contents in the PPy-CuCl₂ catalyst.

Figure 1. Leaching of CuCl₂ (Cu and Cl₂) from PPy.

4. SUMMARY

The new heterogeneous π -conjugated PPy-CuCl₂ catalyst showed high catalytic activity for the DMC synthesis from methanol, CO, and O₂. The catalyst was able to be recycled at least 3 times, keeping its initial catalytic activity. The catalytic activity was much higher than that of the poly(4-vinylpyridine)-CuCl₂ catalyst. The PPy-CuCl₂ catalyst showed excellent corrosion resistance toward stainless steels, compared with the homogeneous CuCl₂ catalyst.

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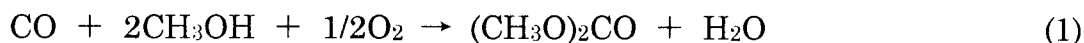
Chapter 6
A New Type of Support
“Bipyridine Containing Aromatic Polyamide” to CuCl_2
for the Synthesis of DMC
by Oxidative Carbonylation of Methanol

ABSTRACT

A new type heterogeneous catalyst, ‘bipyridine containing aromatic polyamide’ (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(4-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 3 times repetition. During the reaction, 20~30 % of total CuCl_2 was eliminated from the immobilized catalyst. Although the leaching 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.

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 produced 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) chloride 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, 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 inside of 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)Cl_2 , 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, 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(4-vinylpyridine) (PVP) has been widely used as a good support and also known as a good support for CuCl_2 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 polymer and shows good heat resistance [10], has been also found to be useful for the DMC synthesis to improve the above problem [in Chapter 4].

The polyamides which possess coordination site have been used as supports for immobilized catalysts [11, 12]. In particular, aromatic polyamides are known to show high heat resistance which is representative to poly(*p*-phenyleneterephthalamide) [13].

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 [14] and liquid-crystalline polymers [15].

We synthesized one of these polyamides (Bpya) (Scheme 1) and found that Bpya is very useful as the support of CuCl_2 , and that the formed CuCl_2 complex (Scheme 2) 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.

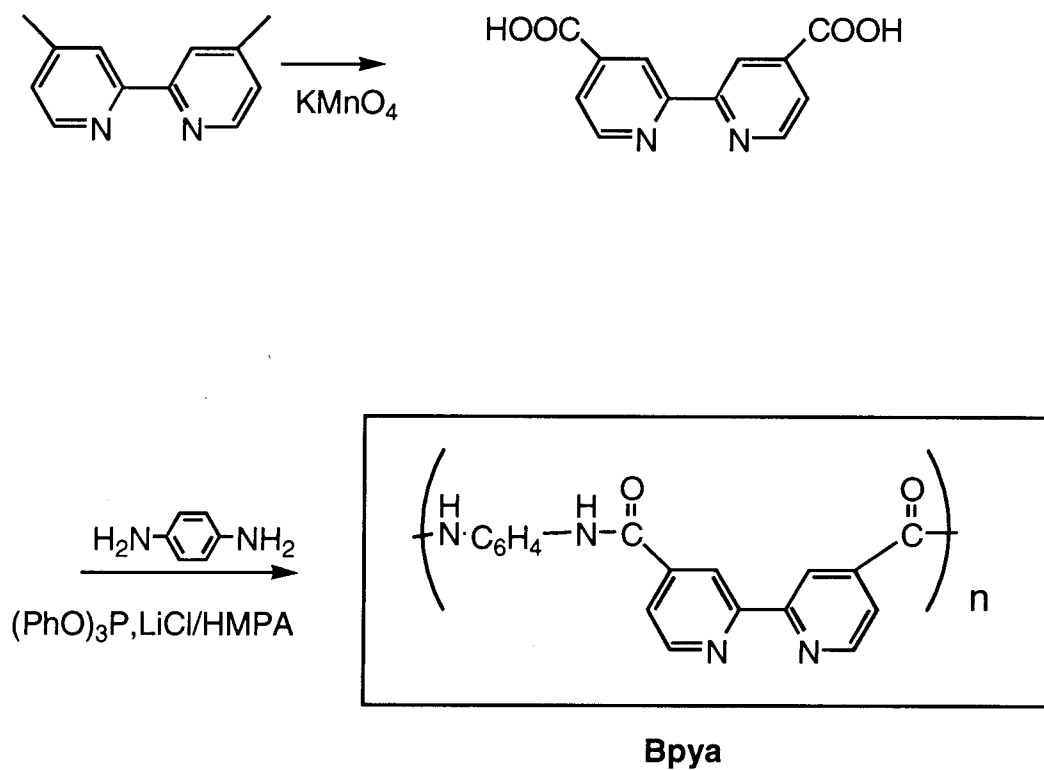
2. EXPERIMENTAL

2.1. Preparation of Poly(*N,N'*-bisphenylene-2,2'-bipyridine-4,4'-dicarboxylic amide) (Bpya)-CuCl₂

Bpya was synthesized by the typical procedure described in the literature (Scheme 1) [14] as follows.

As a pretreatment, crude 4,4'-dimethyl-2,2'-bipyridine (reagent as commercially received) (60 g: 0.326 mol) was dissolved in hot acetone (1680 ml). The solution was added to a K₂CO₃ (18.93 g: 0.137 mol) solution in ice water (4.2 L). After stirring for 10 min, 4,4'-dimethyl-2,2'-bipyridine was precipitated. KMnO₄ (224.6 g) and H₂O (6 L) were refluxed in a 10 L reactor. 4,4'-dimethyl-2,2'-bipyridine in aqueous 20 % KOH (100 ml) (slurry) was gradually added to the reactor, and the mixture was refluxed for 5 h and cooled to room temperature. The precipitated white powder was dissolved in ethyl acetate (1 L), and then precipitated MnO₂ was filtered. 2,2'-bipyridine-4,4'-dicarboxylic acid was extracted from the ethyl acetate layer using water. Aqueous CH₃CO₂H/HCl = 1/1 was added to the solution until pH = 3.5, and the precipitate was washed using H₂O and acetone. The crude product (32.47 g) was obtained. This was washed with CHCl₃/10 % NH₃ in methanol = 3/1, followed by aqueous CH₃CO₂H (pH = 3.5) and water. 2,2'-bipyridine-4,4'-dicarboxylic acid 15.45 g (yield 19.4 %) was obtained. IR (KBr) 2450, 1720, 1370, 1290 cm⁻¹. ¹H-NMR (DCO₂D, 60 MHz) δ 9.4 (br, 4H), 8.5 (d, 2H).

HPLC purity of the product was 94 % (observed wavelength: 210 nm)



Scheme 1. Synthesis of Bpya support.

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} $^1\text{H-NMR}(\text{DCO}_2\text{D}, 60 \text{ MHz})$ 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 %. Calcd. 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 Calcd.) 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 2) can be estimated to be about 15 (Calcd: C, 68.3; H, 3.86; N, 17.51 %).

Bpya powder and the 2 equiv. of CuCl_2 in methanol was 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 mole% 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 %,

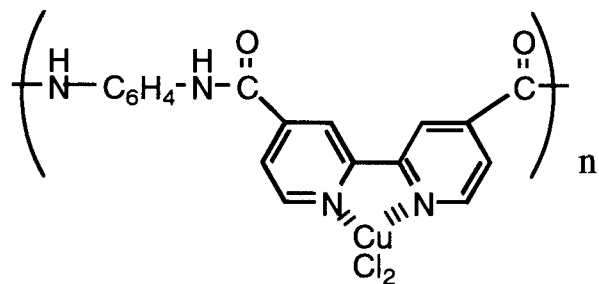
Ni: base; made by Mitsubishi Material Co. Ltd.) autoclave, 10 ml (7.75 g) of methanol was introduced as both substrate and solvent and Bpya-CuCl₂ powder (756 mg) was added ([Cu] = 150 mM), and CO (23 kgf/cm²), O₂ (2 kgf/cm²) was introduced to the vapor phase. After the reaction of 2 h at 140 °C, the concentrations of DMC, methanol, CO₂, and O₂ was analyzed by gas chromatography.

The rate of corrosion originated from each catalyst during the reaction was measured separately by the following experiments. The test pieces (about 15 mm×6 mm×2 mm) of SUS316 (Cr: 18 %, Mo: 2 %, Ni: 10 %, C: 0.08 %, Fe: base, 2.0±0.2 g) and HC276 (3.0±0.3 g) was 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-CuCl₂

The catalytic activity of Bpya-CuCl₂ was studied for the DMC synthesis by oxidative carbonylation of methanol. The methanol conversion, DMC yield based on O₂, and DMC selectivity are listed in Table 1. As references, the data of homogeneous CuCl₂, and poly(4-vinylpyridine) (PVP)-CuCl₂, which is insoluble in methanol, are also listed. All these reactions were carried out under the same reaction conditions, where no by-product except CO₂ was detected by gas chromatography.



Scheme 2. The molecular structure of Bpya-CuCl₂.

Table 1

Catalytic activity of Bpya-CuCl₂ comparing to PVP-CuCl₂ and homogeneous CuCl₂^a.

Catalyst	MeOH conv.	DMC yield	DMC sel.
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 [Cu] = 150 mM, MeOH = 10 ml, CO = 23 kgf/cm², O₂ = 2 kgf/cm²,

Temp. = 140 °C, Reaction time = 2 h.

MeOH conv. (%) = produced DMC/(introduced MeOH/2).

DMC yield (%) = produced DMC/(introduced O₂x2).

DMC sel. (%) = DMC/(DMC + CO₂).

The used PVP is non-crosslinked 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-CuCl₂ was prepared in the same way to Bpya-CuCl₂ and obtained as a green powder; this complex was also insoluble in methanol. The ratio of CuCl₂/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 CuCl₂ catalyst, the methanol conversion of steady state has been usually adjusted to around 5 % [5]. So we carried out the reaction under the lower O₂ 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 [16–22] and, due to the above reason, the DMC yield and selectivity of PVP-CuCl₂ are obviously lower than the homogeneous CuCl₂ (Table 1). The DMC yield and selectivity by using Bpya-CuCl₂ are also lower than those of homogeneous CuCl₂ by the same reason.

The melting point of the synthesized Bpya was confirmed to be beyond 250 °C. It indicates that Bpya-CuCl₂ shows high heat resistance which is one of the important characters of this catalyst. Because of its low melting point of non-crosslinked PVP, it is necessary to carry out the reaction at a lower temperature to keep the stability of the PVP-CuCl₂ catalyst; it has been reported that cross-linked PVP-CuCl₂ is very active and stable for the DMC synthesis up to 140 °C [9].

For the PVP-CuCl₂ catalytic system, after the reaction, a peak at 1597 cm⁻¹ in the IR spectrum which is assigned to ν (C=N) of the pyridine ring coordinated to Cu²⁺ (ν (C=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-CuCl₂ could be recycled after simple filtration. The weight loss of Bpya-CuCl₂ due to the handling during the above procedure is about 10 % of total weight in each time. This includes the loss of CuCl₂ which was eliminated from Bpya support. This loss was compensated by adding the fresh catalyst to adjust the concentration of Cu to be 150 mM.

Figure 1 shows the catalytic performance (DMC yield (a) and DMC selectivity (b)) of Bpya-CuCl₂ for stepwise 3 batch reactions after the process of filtration as mentioned above. Obviously the catalyst kept its initial activities at least 6 h (2 h/for each).

3.2. Rate of Corrosion

The rates of corrosion due to Cl⁻ are listed in Table 2 for Bpya-CuCl₂ and PVP-CuCl₂ (measured after 1st use and 3rd use), as well as homogeneous CuCl₂. 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 CuCl₂ showed very high corrosive character to both SUS316 and HC276. On the other hand, PVP-CuCl₂ and Bpya-CuCl₂ 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, 21, 22]. In this point, therefore, both PVP and Bpya are good supports for corrosive CuCl₂. PVP was sometimes used as a support for homogeneous catalytic systems, and also used for the DMC synthesis by the oxidative carbonylation of

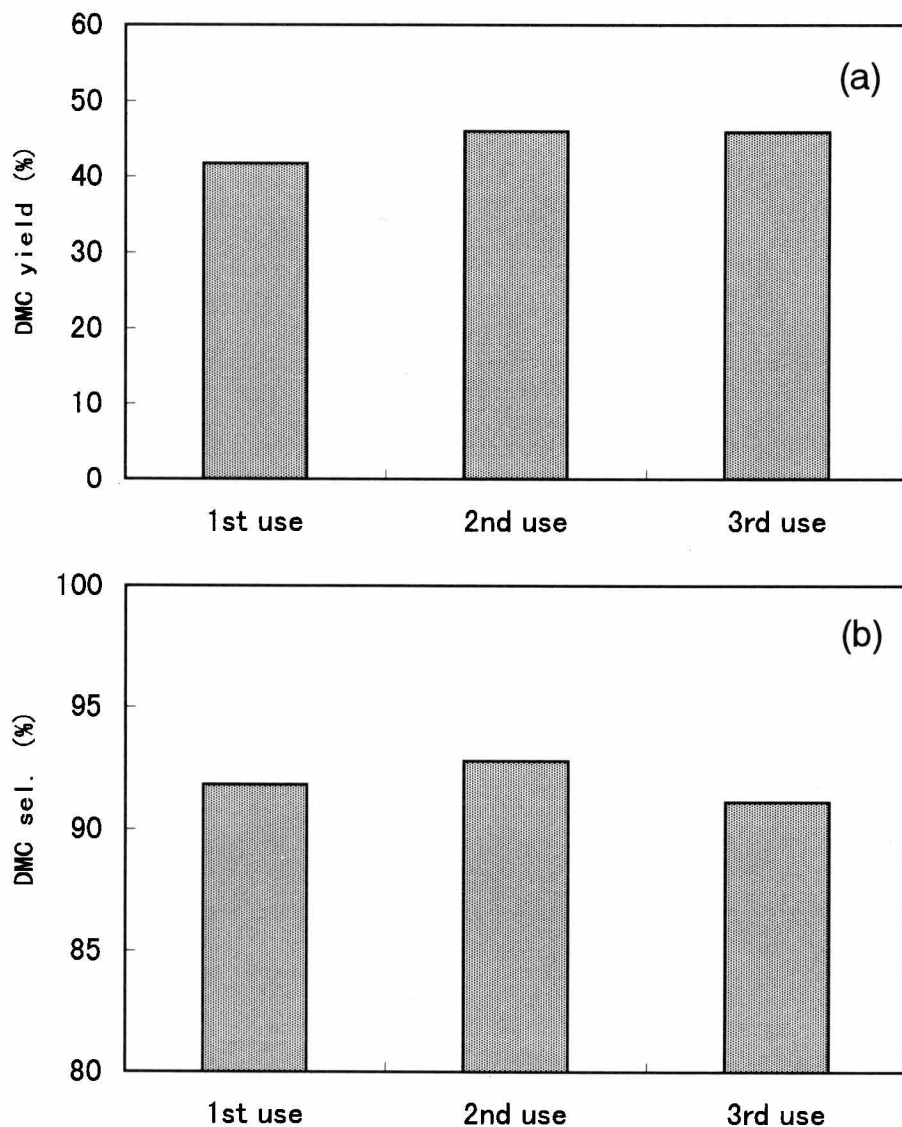


Figure 1. The catalytic activity of recycled Bpya-CuCl₂.

(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 fresh catalyst.

The reaction conditions are given in the footnote of Table 1.

methanol. Our data are in accordance with the previous report that PVP-CuCl₂ shows good activity and remarkably improves the corrosive character of Cl⁻ [21, 22].

It is notable that Bpya-CuCl₂ also showed catalytic activity for DMC synthesis, and that the corrosive character was also reduced remarkably. For both Bpya-CuCl₂ and PVP-CuCl₂, the recycled catalyst showed better corrosive character than their 1st use.

However, some pitting corrosion which can not be clearly estimated from the loss of weight was observed for both catalysts. This was observed at higher density for SUS316 than for HC276 (Figure 2) in each case. So it is clear that SUS316 and HC276 can not be used industrially as a material of the reactor, and the glass lining is necessary. However, the danger for cracking of the glass which will cause sudden explosion may prefer 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 Figure 3. 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 [23].

So it is reasonable to consider that some of the coordinated Cl⁻ are exchanged with another ligand. From Figure 3, 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).

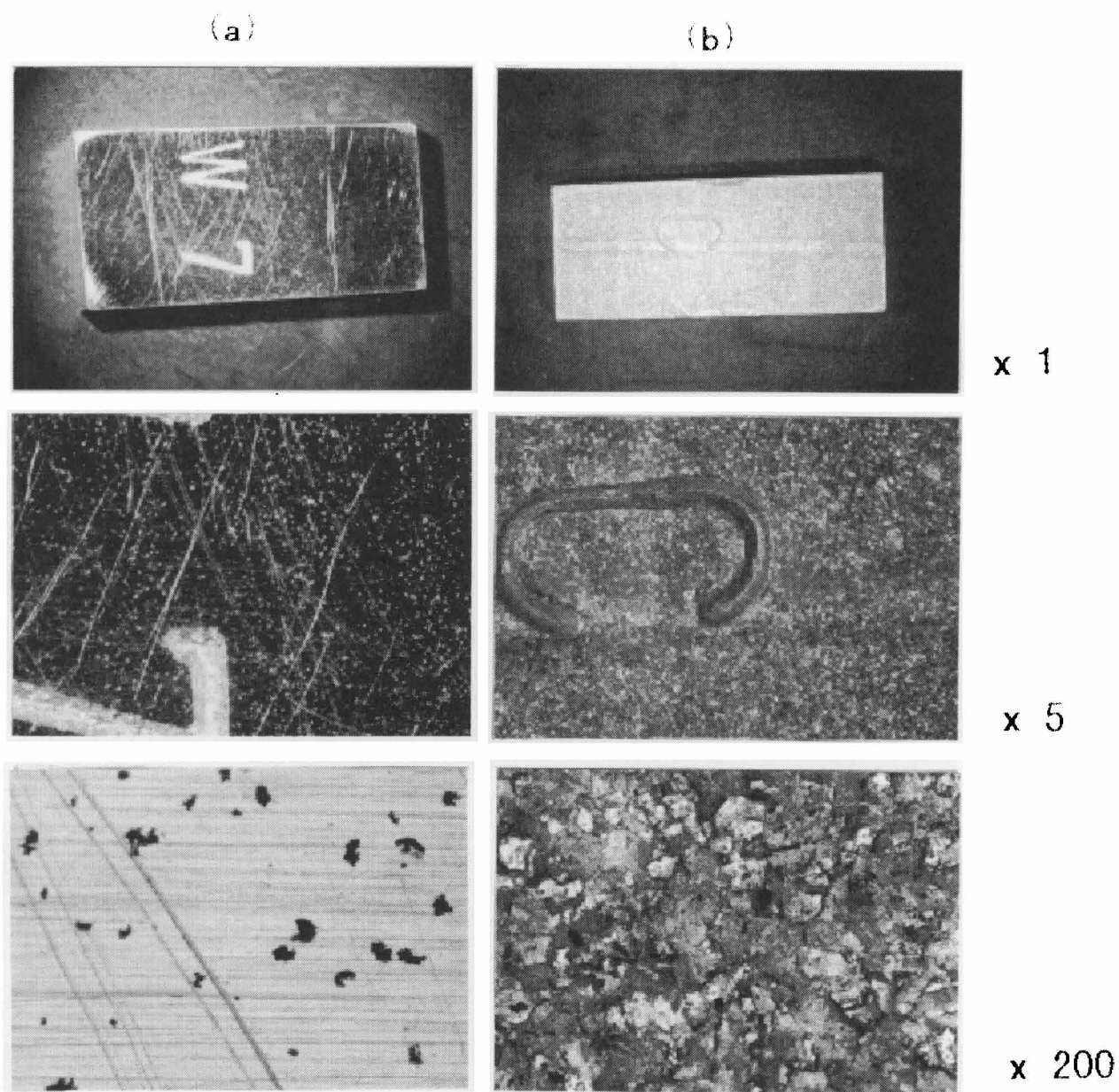


Figure 2. Pitting corrosion, observed for the surface of HC276 test pieces. (a) using Bpya- CuCl_2 catalyst (in the recycled use); (b) using homogeneous CuCl_2 catalyst.

Table 2

Rate of corrosion due to Cl^- for Bpya- CuCl_2 , comparing to PVP- CuCl_2 and homogeneous CuCl_2 ^a.

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.

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

^c Within the limit of detection.

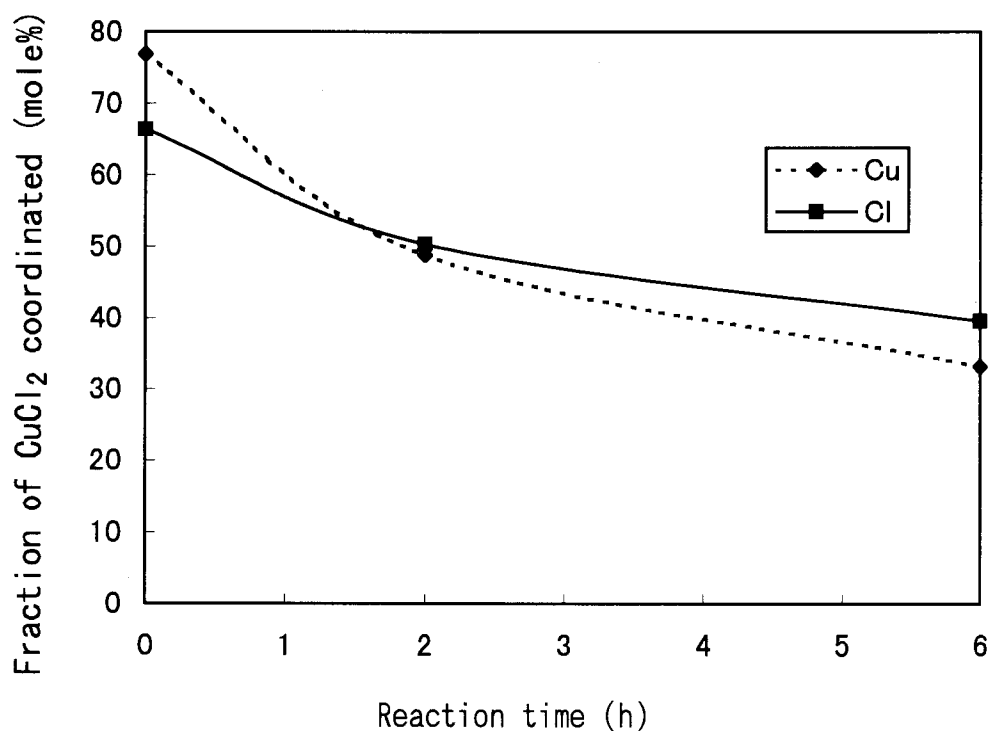
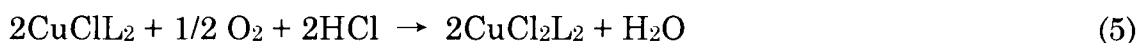
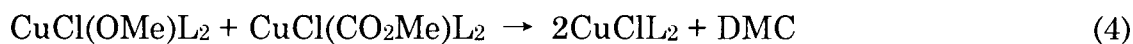
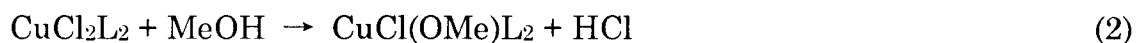


Figure 3. The fraction of CuCl_2 coordinated with Bpya before and after the reaction. Reaction conditions are given in Table 1-3.

3.3. Reaction Mechanism

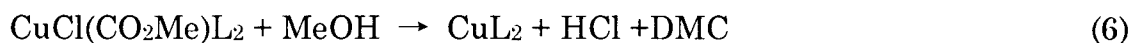
For the synthesis of one DMC molecule, two-electron transfer is necessary. It has been considered that two types of Cu(I)/Cu(II) redox couples are included in the reaction mechanism of DMC synthesis with Cu(I)Cl catalytic system [23]. In this cycle, the active species has been supposed to be CuCl(OMe). Equations (2)~(5) represents a Cu(I)/Cu(II) redox system for the Cu(II)Cl₂ catalytic system.



(L: pyridyl unit in bpy)

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 the two Cu(II) species in eq.(4) 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. 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 (eq.(6)).



Cu(0) possesses 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, the Cu(0) intermediate 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 [24]

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- CuCl_2 and Bpya- CuCl_2 , the opportunity for the two Cu(II) intermediates to interact is much lower than in the case of an homogeneous CuCl_2 catalytic system. However, we consider that the Cu(II)/Cu(I) redox cycle is predominant because no Cu(0) species could be detected from the XPS study for the Pvbpy- CuCl_2 catalyst [in Chapter 2].

4. SUMMARY

A new heterogeneous catalyst Bpya- CuCl_2 was studied for DMC synthesis by oxidative carbonylation of methanol. This catalyst showed activity almost equal to that of PVP- CuCl_2 . Bpya- CuCl_2 could be recycled at least 3 times, keeping its initial reactivity. Bpya- CuCl_2 showed good corrosion resistance to HC276 as in the case of PVP- CuCl_2 . The results were considered from the viewpoint of two types of reaction mechanisms.

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CONCLUSIONS

We investigated a novel type of heterogenized catalysts, namely, polymer-bound Cu complexes for the oxidative carbonylation of methanol as an alternative for a CuCl_2 catalyst in the liquid-phase reaction. The polymer supports are different in their coordination sites (bidentate 2,2'-bipyridine, oxine, and monodentate pyridine), bond types (coordinate, ionic), and polymer types (π -conjugated, aramid, polyvinyl). These characteristics cause differences in their own physical properties (stability constant to metals, heat-resistance, etc.).

In Chapters 2 and 3, we focused on the differences of coordination sites (O-Cu ionic, N-Cu coordinate) of catalysts whose polymer chain is characterized by the polyvinyl type.

In Chapter 2, a polymer including 2,2'-bipyridine, poly(4-methyl-4'-vinyl-2,2'-bipyridine) (Pvbpy) was investigated as a support for CuCl_2 . The Pvbpy- CuCl_2 catalyst showed considerable catalytic activity, comparable to that of the poly(4-vinylpyridine) (PVP)- CuCl_2 catalyst; the Pvbpy- CuCl_2 catalyst could be recycled after filtration and washing three times provided that it had not lost activity. The corrosion originating from Cl^- was greatly improved by immobilizing the CuCl_2 by Pvbpy. However, leaching of CuCl_2 from the Pvbpy- CuCl_2 catalyst was observed during the reaction. In the first reaction, about 38 % of the initially supported Cl was released, and in the second and third reactions, most of the Cl was retained. The rate of corrosion of stainless steels in the first use of the catalyst was greater than that in the rate of the second and third uses. These results are closely related to the amount of Cl^- released from the Pvbpy- CuCl_2 catalyst, which demonstrates that the main cause of corrosion in the catalytic system is Cl^- released from the Pvbpy- CuCl_2 catalyst. From an XPS study of the catalyst, it became obvious that Cu(II) was gradually reduced to Cu(I) during the reaction.

In Chapter 3, we synthesized novel immobilized CuCl_2 catalysts ($\text{Cu}(\text{ox})_2$, $\text{Cu}(\text{ox})\text{Cl}$ (oxH = 8-quinolinol), and PVO-Cu ; PVO is a co-polymer of 2-vinyl-8-quinolinol with styrene), which include 8-quinolinol as a coordination site. These three types of immobilized catalysts include Cl with various ratio per Cu , and the catalytic activities were found to be lower than those of the Pvbpy-CuCl_2 catalyst and closely related to the Cl/Cu mol ratio in the catalysts. $\text{Cu}(\text{ox})_2$ which includes no Cl , showed no reaction activity in the DMC synthesis. Therefore, Cl^- is necessary for the catalytic systems. This is in accordance with the reaction mechanism previously proposed for DMC synthesis using a CuCl catalyst, in which Cl^- plays an important role for the redox cycle of Cu(II)/Cu(I) to produce DMC. The catalytic activities of $\text{Cu}(\text{ox})\text{Cl}$ and PVO-Cu became lower than those of the homogeneous CuCl_2 catalyst. This is due to the lower Cl/Cu mol ratio of the catalysts compared to CuCl_2 , in addition to the ordinary demerit of immobilization. The relation of catalytic activities to the Cl/Cu mol ratio was studied for the above catalysts, and it was observed that DMC selectivity became higher according to the increase of Cl/Cu .

In Chapters 4 to 6, we focussed on the differences of polymerization types (polyamide, π -conjugation) among catalysts whose coordination type is the N-Cu coordination of pyridine ring.

In Chapter 4, we synthesized the π -conjugated poly(2,2'-bipyridine-5,5'-diyl) (PBpy) - CuCl_2 complex and investigated its catalytic activity by using this. The higher DMC yield and DMC selectivity was observed than those of the similar heterogeneous PVP-CuCl_2 catalyst. The high catalytic activity is associated with the π -conjugated conductive properties of the supporting ligand, PBpy . The PBpy-CuCl_2 catalyst can be easily recycled after filtration, and the catalytic activity is maintained after being used three times. The PBpy-CuCl_2 catalyst is much less corrosive toward stainless steels compared with PVP-CuCl_2 and the ligand-free CuCl_2 catalyst.

In Chapter 5, poly(pyridine-2,5-diyl) (PPy), which has nonodentate

pyridine as its coordination site and a similar π -conjugated system, was investigated as a support for CuCl_2 . The PPy- CuCl_2 adduct also had high catalytic activity. The adduct caused the corrosion of stainless steel vessels only to a minor extent compared with the homogeneous CuCl_2 catalyst. This PPy- CuCl_2 catalyst was easily recycled by filtration and showed similar catalytic activity in the third use. The presence of a π -conjugated system in PPy, through which electrons can move, may also bring high catalytic activity for the oxidative carbonylation of methanol, which involves Cu(II)/Cu(I) redox processes.

In Chapter 6, a new type of heterogeneous catalyst, "bipyridine containing aromatic polyamide" (Bpya)- CuCl_2 , was investigated. This catalyst showed good performance (high DMC yield and DMC selectivity), as in the case of PVP- CuCl_2 . Bpya showed higher heat resistance than PVP, and thus Bpya- CuCl_2 was 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 3 repetitions. During the reaction, some CuCl_2 was eliminated from the immobilized catalyst. Although considerable leaching of CuCl_2 was observed in the initial step, it became slight during the reaction. The characteristics of corrosion resistance of Bpya- CuCl_2 were studied, and it became obvious that corrosion is closely related to the trend of CuCl_2 elimination.

In summary, the Cu(II)-polymer complexes in this research exhibited considerable catalytic activities and stability for DMC synthesis as heterogenized catalysts as well as low corrosivity to stainless steels. In particular, the PBpy- CuCl_2 catalyst, which has a π -conjugation system through the polymer-chain and the bidentate coordination sites of the 2,2'-bipyridine unit, showed a high DMC yield and selectivity comparable to those of the homogeneous CuCl_2 catalyst. It can be concluded that the π -conjugation system plays an important role in promoting the catalytic reaction, including the redox of the coordinated metals. The PPy- CuCl_2

catalyst, whose coordination site is considered to be mostly monodentate pyridine, exhibited some release of initially coordinated Cu atom, while the PBpy-CuCl₂ catalyst exhibited almost no leaching of Cu during the reaction.

To explain the high catalytic activity and high stability of the PBpy-CuCl₂ catalyst, MO calculations were performed for the PBpy support, and it was indicated that, in order to expand the π -conjugation system of the polymer, the LUMO energy gradually falls off, resulting in the increase of the importance of the π -back donation effect to the binding force toward Cu. Thus, the high binding ability of the polymer support by its chelation and the conductivity of the polymer support are effective for this type of catalyst design.

We have presented an effective approach for designing the support for the liquid-phase reaction in the DMC synthesis reaction, comparing the catalytic properties of each catalyst deriving from a molecular structure different from that of the supports, and suggested that both of the electronic structure and coordination ability of the polymer support are important for the development of an effective catalytic system.

List of Publications

1. Y. Sato, M. Kagotani, T. Yamamoto, Y. Souma
"Novel Effective Poly(2,2'-bipyridine-5,5'-diyl)-CuCl₂ Catalyst for Synthesis of Dimethyl Carbonate (DMC) by Oxidative Carbonylation of Methanol"
Applied Catalysis A: General, **185**, 219–226 (1999).
2. Y. Sato, M. Kagotani, Y. Souma
"A New Type of Support "Bipyridine Containing Aromatic Polyamide" to CuCl₂ for Synthesis of Dimethyl Carbonate (DMC) by Oxidative Carbonylation of Methanol"
Journal of Molecular Catalysis A: Chemical, **151**, 79–85 (2000).
3. Y. Sato, M. Kagotani, Y. Souma
"Synthesis of Dimethyl Carbonate (DMC) by Oxidative Carbonylation of Methanol using Polymer-supported CuCl₂ Catalyst"
Journal of The Japan Petroleum Institute, **43**(1), 75–79 (2000).
4. Y. Sato, Y. Souma
"Design of Novel Immobilized Catalyst for Dimethyl Carbonate Synthesis"
Syokubai, **42**(1), 36–39 (2000) [in Japanese].
5. Y. Sato, T. Yamamoto, Y. Souma
"Poly(pyridine-2,5-diyl) - CuCl₂ Catalyst for Synthesis of Dimethyl Carbonate by Oxidative Carbonylation of Methanol: Catalytic Activity and Corrosion Influence"
Catalysis. Letters, **65**, 123–126 (2000).

6. Y. Sato, Y. Souma

“Novel Type of Heterogenized CuCl₂ Catalytic Systems for Oxidative Carbonylation of Methanol”

Catalysis Surveys from Japan, **4**(1), 65-74 (2000).

Other publication not included in this thesis

Y. Sato, M. Morimoto, H. Segawa, T. Shimidzu

“Twisted Intramolecular Charge-Transfer State of a Donor-Acceptor Molecular System”

Journal of Physical Chemistry, **99**(1), 35-39 (1995).

List of Presentations

1. Y. Sato, M. Kagotani, Y. Souma

“Effective Heterogeneous Catalysts for Synthesis of Dimethyl Carbonate”

9th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (Elsevier Science)

Southampton, UK, 1998/7/23.

2. Y. Sato

“Heterogenization of Homogeneous Metal-Complex Catalyst”

3rd Symposium on Development of New Chemical Technology (Japan Chemical Industry Association)

Tokyo, 1998/11/11.

3. Y. Sato

“Heterogenization of Homogeneous Metal-Complex Catalytic Systems”

4th Symposium on Development of New Chemical Technology (Japan Chemical Industry Association)

Tokyo, 1999/3/26.

4. Y. Sato

“Synthesis of Dimethyl Carbonate using Novel Immobilized Catalytic Systems”(G208)

32th Autumn Meeting of the Society of Chemical Engineers. Japan
Kanazawa, 1999/9/26.

5. Y. Sato

“Development of the Novel Immobilized Metal Complex Catalyst”

4th Meeting of the Organometallic Group in Kinki Chemical Society

Osaka, 2000/3/3.

6. Y. Sato, H. Kojima

“Trial to Immobilize CuCl_2 Catalyst for Dimethyl Carbonate Synthesis”

Organometallic Seminar XXII (Catalyst Society of Japan)

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