

A novel homogeneous catalyst made of poly(*N*-vinyl-2-pyrrolidone)-CuCl₂ complex for the oxidative carbonylation of methanol to dimethyl carbonate

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Abstract

A new type of homogeneous catalyst for dimethyl carbonate (DMC) synthesis by oxidative carbonylation of methanol in the liquid-phase reaction was investigated. The polymer-bound monometallic PVP-CuCl₂ catalyst (PVP, poly(*N*-vinyl-2-pyrrolidone)) prepared by the combination of an alcoholic solutions of PVP and CuCl₂ exhibits excellent catalytic performance for the oxidative carbonylation of methanol with carbon monoxide and oxygen to DMC under 3.0 MPa ($P_{O_2} = 0.24$ MPa and $P_{CO} = 2.76$ MPa) pressure at temperature around 140–160 °C. The catalyst exhibits much higher activity and selectivity than non-supported CuCl₂ in the DMC synthesis reaction. The remarkable increase in the conversion and selectivity is attributed to the presence of a strong complexation effect between Cu(II) and the amide ligands in the polymer chains. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer-bound monometallic catalyst; Oxidative carbonylation; Dimethyl carbonate (DMC); Complexation

1. Introduction

Dimethyl carbonate (DMC) is an environmental benign chemical compound and unique intermediate with versatile chemical reactivity which has attracted increasing interest from both practical and fundamental point of view in recent years [1–3]. DMC is promising to replace the notorious phosgene in many organic synthesis, which is also used as a starting material for polycarbonate, as an additive to gasoline, as a methylating and carbonylating reagent and for other useful applications [2]. Conventionally, the commercial DMC was mainly manufactured by the

reaction of methanol with phosgene and this method suffers from safety problems, as well as numerous environmental problems due to the use of highly toxic phosgene and the co-production of large amount of hydrochloric acid. With increasing demands for a safer and environmentally favorable process for DMC synthesis, it has been of great interest to develop alternative synthetic processes to prepare DMC without using phosgene in the past decades [4–12].

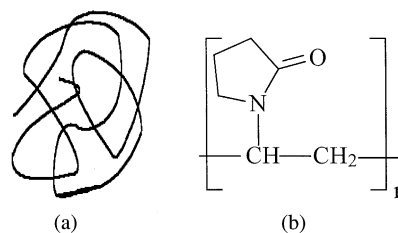
Several phosgene-free approaches have been known for DMC production so far. Among them, the direct oxidative carbonylation of methanol with CO and O₂ has shown to be the most promising processes for the production of DMC. Both homogeneous and heterogeneous catalyst systems using a variety of transition metal containing complexes, transition metal-zeolites, or solid-supported metals have been extensively

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investigated [13–18]. Among various transition metals employed for the oxidative carbonylation of methanol, the simple salt of copper (I and II) chlorides are known as effective catalysts to produce DMC by the oxidative carbonylation of methanol. As an alternative to the commercial CuCl slurry catalyst system employed, numerous attempts have been made to utilize a homogeneous CuCl₂ catalyst in the oxidative carbonylation of methanol to DMC.

It is well known that the catalytic activity and the selectivity of a homogeneous CuCl₂ catalyst are much inferior to those of a slurry CuCl catalyst system. Hence, it is highly attractive to develop new homogeneous copper-based catalytic systems with significantly improved catalytic properties. Recently, homogeneous transition metallic-complex catalysts have attracted considerable attention because their high activity and selectivity in many reactions by means of the addition of various useful organic molecular ligand or polymeric ligand systems [19–22]. The enhanced activity and better selectivity are described to be due to the ligand interaction between the molecular or polymeric ligands and transition metallic species. Very recently, Chin et al. [16] have reported a three-component homogeneous catalyst system consisting of PdCl₂-(PPh₃)₂/Cu(OMe)₂/Me₄NCl for the oxidative carbonylation of methanol to DMC. It was shown that this particular three-component catalyst system can provide a high conversion of methanol in the oxidative carbonylation reaction, but one shortcoming of this complex system is the relatively low selectivity due to the formation of unattractive dimethyl oxalates by the introduction of palladium species.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) was also reported to be promising polymeric ligand system for significant enhancing the efficiency of the oxidative carbonylation of amine or phenol to their corresponding esters [23–25]. The promotion effect of PVP has been attributed to the formation of the PVP complex in the cation forms due to the coordination of the catalyst components to the pendant pyrrolidone groups in PVP (Scheme 1). We now report the new homogeneous polymer-bound monometallic catalyst system consisting of PVP-CuCl₂ for the oxidative carbonylation of methanol in liquid-phase, which produces DMC in relatively high yield and selectivity. By means of the addition of PVP as a polymeric ligand system, we



Scheme 1. The molecular structure of poly(*N*-vinyl-2-pyrrolidone) (PVP).

found that the PVP polymer can remarkably increase the catalytic activity and selectivity of the conventional CuCl₂ catalyst system. The effect of the addition of PVP as a polymeric ligand, as well as various operation variables is also investigated in the present work.

2. Experimental

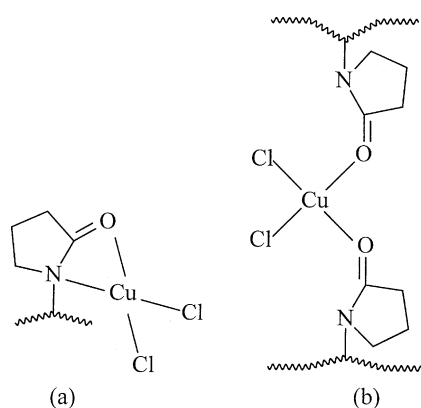
2.1. Reagents and materials

CuCl₂·2H₂O (Aldrich) and methanol (>99.8%, analytical grade) were used as purchased. PVP (*K* = 27–33) was purchased from BASF. Carbon monoxide with a purity of 99.999% and oxygen with a purity of 99.9% were purchased from BOC gas.

2.2. Catalyst preparation and characterization

To a stirred mixture of CuCl₂·2H₂O in methanol, a second solution of methanol containing appropriate amount of PVP were added successively. After the mixture of PVP-CuCl₂ (5×10^{-2} mmol Cu/ml, N/Cu = 1, 2, 4, 6, 8, respectively) was stirred at room temperature for 0.5 h, it was heated to 80 °C and stirred for another 10 h under reflux. The resultant polymer-bound monometallic PVP-CuCl₂ catalyst in powder form was finally obtained (Scheme 2) by solvent evaporation.

Infrared (IR) spectra were recorded using a Bruker Vector 22 FTIR spectrometer equipped with a DTGS detector and a KBr beam splitter. The X-ray photoelectron spectra (XPS) of the PVP-CuCl₂ complexes were carried out in a Perkin-Elmer PHI 5000C ESCA system using Al K α radiation (1486.6 eV).



Scheme 2. Schematic models of CuCl_2 complexed to polymeric PVP ligands: (a) Cu(II) ion anchored to the oxygen and nitrogen atoms in one amide moiety; (b) Cu(II) ion coordinated to two carbonyl oxygen atoms from two neighboring amide ligands.

2.3. Catalytic reaction

The catalytic oxidative carbonylation of methanol was carried out in an internal Teflon[®] lined with stainless steel autoclave of 135 ml, equipped with a magnetic stirrer. A typical procedure for the catalytic DMC synthesis was conducted as follows: in to the autoclave, 10 ml of methanol and the powdered polymer-bound monometallic catalyst PVP- CuCl_2 were charged (if no specification, $[\text{Cu}^{2+}] = 180 \text{ mM}$). Then, O_2 ($P_{\text{O}_2} = 0.24 \text{ MPa}$) and CO ($P_{\text{CO}} = 2.76 \text{ MPa}$) were introduced. After carrying out the reaction at temperature around 140°C for 1–7 h, the amounts of DMC, methanol, CO , CO_2 and O_2 were analyzed by gas chromatography.

3. Results and discussion

3.1. Efficiency of the poly(*N*-vinyl-2-pyrrolidone)- CuCl_2 catalyst with various N/Cu ratio

To investigate the role of PVP addition to the catalytic properties of the PVP- CuCl_2 , the oxidative carbonylation of methanol with CO and O_2 to DMC with various N/Cu mole ratio has been carried out. The data for the production of DMC with MeOH , CO and O_2 as a function of catalyst composition are given in Table 1. It is shown that the monometallic CuCl_2 catalyst in the absence of PVP has exhibited a moderate catalytic activity. However, it is found that the DMC can be produced in a remarkably high yield with extremely high selectivity from the oxidative carbonylation of MeOH over the polymer-bound PVP- CuCl_2 catalytic systems.

In the presence of PVP, all resultant reaction mixtures seemed to be homogeneous viscous liquids and both the rate and yield of reaction catalyzed by CuCl_2 were greatly enhanced by the complexation of PVP. As shown in Table 1, the CuCl_2 catalyst without PVP complexation can only afford a methanol conversion of 3.68% at a selectivity of 95.7% based on methanol. The yield of DMC is about 4.87 wt.% in the liquid product after a reaction time of 5 h. Both the conversion of methanol and the selectivity to DMC are greatly increased upon the introduction of PVP, showing a strong promotional effect on the CuCl_2 in the DMC synthesis reaction. Table 1 shows that a maximum DMC concentration in the liquid products and a much lower carbon dioxide concentration in gas prod-

Table 1
Catalytic activities of the PVP- CuCl_2 with different N/Cu molar ratio in DMC synthesis

Catalyst N/Cu	$\text{CH}_3\text{OH}^{\text{a}}$ conversion	DMC (mass%)	DMC ^b selectivity (CH_3OH)	DMC ^c yield (O_2)	DMC ^d selectivity (O_2)
0	3.68	4.87	95.76	18	97.3
1	8.76	10.65	99.30	44	98.2
2	12.09	16.28	98.30	61	98.7
4	11.54	15.35	99.09	58	98.3
6	11.51	15.33	99.21	58	98.2
8	11.46	15.30	99.51	58	98.0

Reaction conditions: $[\text{Cu}^{2+}] = 400 \text{ mM}$, $P_{\text{O}_2} = 0.24 \text{ MPa}$, $P_{\text{CO}} = 2.76 \text{ MPa}$, $t = 5 \text{ h}$, $T = 120^\circ\text{C}$.

^a MeOH conversion (%) = 2 produced DMC/introduced MeOH .

^b DMC selectivity (MeOH , %) = 2 produced DMC/reacted MeOH .

^c DMC yield (O_2 , %) = produced DMC/2 introduced O_2 .

^d DMC selectivity (O_2 , %) = produced DMC/(produced DMC + produced CO_2).

ucts was achieved on the PVP-CuCl₂ catalyst when N/Cu mole ratio was 2. The conversion of methanol for the PVP-CuCl₂ catalyst with N/Cu mole ratio of 2 is more than three times of that for CuCl₂ and the selectivity is also significantly improved. The maximum DMC concentration in the liquid products can attain 20.24 wt.% after a 5 h reaction. The dramatic increase in both the catalytic activity and selectivity may be understood by considering that the Cu(II) species in the PVP-CuCl₂ complex were strongly coordinated to amide moieties in PVP, which give rise to an increase in the reaction efficiency. With a further increase in N/Cu ratio, DMC concentration in liquid products decreased slightly while carbon dioxide concentration in gas products changed in a reverse way.

It is noticeable that the PVP-CuCl₂ catalyst with N/Cu mole ratio of 2/1 showed the highest catalytic activity. We suggest that in the case of using insufficient amount of PVP, only the well-coordinated Cu(II) species will coordinate PVP. However, in the case of excess amount of PVP, the PVP chain that could not coordinate to Cu(II) species will cover the surface of the polymer-bound catalyst to prevent the interaction of the catalyst components with methanol, CO and oxygen. This may well account the experimental fact that in the presence of either excess or insufficient amount of PVP, the efficiency of the CuCl₂ catalyst was reduced.

3.2. Effect of reaction conditions on the catalytic activities

To gain further understanding on the catalytic performance of the polymer-bound PVP-CuCl₂ cat-

alytic systems, the effect of the reaction time on the oxidative carbonylation of methanol to DMC in liquid-phase was studied. Since the PVP-CuCl₂ catalytic system with N/Cu mole ratio of 2 has demonstrated the best catalytic performance in the oxidative carbonylation of methanol with CO and O₂ to produce DMC, the experiments have been focused on the polymer-bound catalyst with N/Cu mole ratio equals to 2/1. The effect of reaction time on the catalytic activities of the PVP-CuCl₂ catalyst with N/Cu ratio of 2/1 in DMC synthesis is summarized in Table 2. Reactions were carried out at temperature of 120 °C with the copper concentration of 400 mM [Cu²⁺] under a total pressure of 3 MPa ($P_{O_2} = 0.24$ MPa, $P_{CO} = 2.76$ MPa). It is seen that the reaction time has a strong influence on the yield of DMC in the oxidative carbonylation of methanol. There is an almost linear increase of the methanol conversion, as well as the DMC concentration in the liquid products with increasing reaction time if the time is less than 4 h. It is noticeable that there is no CO₂ formation based on the gas product analysis for the reaction time less than 4 h, indicating the extremely high selectivity of the novel polymer-bound PVP-CuCl₂ catalytic system in DMC synthesis. The DMC yield is found to approach the maximum value when the reaction is carried out for 5 h. Further reaction only results in a slight decrease in the yield of DMC presumably due to the deep oxidation caused by prolonged reaction under oxygenated atmosphere.

The effect of the amount of PVP-CuCl₂ complex on the efficiency of the oxidative carbonylation reaction was investigated in an effort to determine the optimal reaction conditions. The reaction for the PVP-CuCl₂

Table 2
Effect of reaction time for catalytic activity of the PVP-CuCl₂ with ratio of N/Cu 2 in DMC synthesis

Reaction time (min)	CH ₃ OH ^a conversion	DMC (mass%)	DMC ^b selectivity (CH ₃ OH)	DMC ^c yield (O ₂)	DMC ^d selectivity (O ₂)
60	3.65	5.26	≈100	19	≈100
120	5.02	6.91	≈100	26	≈100
240	10.09	13.60	98.30	52	99.5
300	12.09	16.27	98.28	61	98.7
420	12.02	16.17	98.20	60	98.6

Reaction conditions: [Cu²⁺] = 400 mM, $P_{O_2} = 0.24$ MPa, $P_{CO} = 2.76$ MPa, $T = 120$ °C.

^a MeOH conversion (%) = 2 produced DMC/introduced MeOH.

^b DMC selectivity (MeOH, %) = 2 produced DMC/reacted MeOH.

^c DMC yield (O₂, %) = produced DMC/2 introduced O₂.

^d DMC selectivity (O₂, %) = produced DMC/(produced DMC + produced CO₂).

Table 3

Effect of the amount of catalyst for catalytic activity of the PVP-CuCl₂ with ratio of N/Cu 2 in DMC synthesis

Catalyst [Cu ²⁺]	CH ₃ OH ^a conversion	DMC (mass%)	DMC ^b selectivity (CH ₃ OH)	DMC ^c yield (O ₂)	DMC ^d selectivity (O ₂)
400	12.09	16.28	98.30	61	98.7
250	12.42	16.64	99.73	64	98.9
180	12.68	16.98	99.78	65	99.8
100	7.93	10.82	99.81	41	99.6

Reaction conditions: $P_{O_2} = 0.24$ MPa, $P_{CO} = 2.76$ MPa, $t = 5$ h, $T = 120$ °C.^a MeOH conversion (%) = 2 produced DMC/introduced MeOH.^b DMC selectivity (MeOH, %) = 2 produced DMC/reacted MeOH.^c DMC yield (O₂, %) = produced DMC/2 introduced O₂.^d DMC selectivity (O₂, %) = produced DMC/(produced DMC + produced CO₂).

catalyst with N/Cu mole ratio of 2/1 was conducted under 3.0 MPa pressure at temperature of 120 °C for 5 h. The partial pressure for O₂ and CO are maintained at $P_{O_2} = 0.24$ MPa and $P_{CO} = 2.76$ MPa, respectively. The detailed results for the PVP-CuCl₂ (N/Cu = 2/1) catalyst with various copper concentrations were presented in Table 3. It is shown that even at the low catalyst concentration of 100 mM, a good DMC yield can be obtained over the PVP-CuCl₂ catalyst. Increasing the concentration of the catalyst can greatly enhance the DMC concentration in the liquid products. The optimum concentration of the polymer-bound catalyst is 180 mM, where the DMC can be obtained in yield of 16.98 wt.% with a high selectivity based on both methanol and CO conversion. For the case with excess amount of the catalyst, the efficiency of the catalyst went slightly down due to the heavier viscous nature of the homogeneous reaction system that may inhibit the facile interaction between the catalytic components and the reactants of methanol, CO and O₂.

The effect of reaction temperature on the DMC production over the polymer-bound PVP-CuCl₂ (N/Cu = 2/1) catalyst was also examined over a wide reaction temperature ranging from 100 to 180 °C. The results obtained at 3.0 MPa pressure ($P_{O_2} = 0.24$ MPa, $P_{CO} = 2.76$ MPa) with copper concentration of 180 mM [Cu²⁺] for a 5 h reaction were shown in Table 4. It is demonstrated that the yield of DMC is a strong function of the reaction temperature. At 100 °C, the DMC concentration in the liquid products is very low due to the slow reaction rate at a low reaction temperature. Upon raising the temperature to above 120 °C, there is a significant increase in the DMC formation according to the data in Table 4. The highest DMC mass concentration of 20.24 wt.% in the liquid product has been attained at the temperature of 160 °C. Further increasing the temperature results in a decrease in DMC formation presumably due to the partial decomposition of DMC at elevated temperature in the reaction system.

Table 4

Effect of reaction temperature for catalytic activity of the PVP-CuCl₂ with ratio of N/Cu 2 in DMC synthesis

Temperature (°C)	CH ₃ OH ^a conversion	DMC (mass%)	DMC ^b selectivity (CH ₃ OH)	DMC ^c yield (O ₂)	DMC ^d selectivity (O ₂)
100	5.9	8.05	98.95	30	99.97
120	12.7	16.98	99.78	65	99.85
140	14.63	19.0	97.97	74	99.57
160	15.48	20.24	98.80	78	99.63
180	14.61	18.95	97.84	74	99.51

Reaction conditions: [Cu²⁺] = 180 mM, $P_{O_2} = 0.24$ MPa, $P_{CO} = 2.76$ MPa, $t = 5$ h.^a MeOH conversion (%) = 2 produced DMC/introduced MeOH.^b DMC selectivity (MeOH, %) = 2 produced DMC/reacted MeOH.^c DMC yield (O₂, %) = produced DMC/2 introduced O₂.^d DMC selectivity (O₂, %) = produced DMC/(produced DMC + produced CO₂).

Table 5
XPS data for PVP, CuCl₂, and PVP-CuCl₂ (N/Cu = 2/1)

XPS peak	Binding energy (eV)		
	PVP	CuCl ₂	PVP-CuCl ₂
N _{1s}	398.95	–	399.35
O _{1s}	530.48	–	531.22
Cl _{2p}	–	199.08	198.56
Cu _{2p_{3/2}}	–	935.01	932.10, 934.01

3.3. Characterization of the PVP-CuCl₂ complex system

The nature of the modification effect of polymeric PVP on the Cu(II) ions and the possible molecular structure of the unique polymer-bound PVP-CuCl₂ catalytic systems in the oxidative carbonylation of methanol with carbon monoxide and oxygen have been investigated by means of combined spectroscopic characterization using XPS and IR techniques.

Table 5 shows the XPS data for PVP, CuCl₂, and the PVP-CuCl₂ (N/Cu = 2) complex. It can be seen that the binding energies of N_{1s} and O_{1s} in PVP-CuCl₂ are 399.35 and 531.22 eV, respectively, which are higher than those in PVP. The difference of Cl_{2p} binding energies between PVP-CuCl₂ and CuCl₂ is 0.52 eV. The Cu_{2p_{3/2}} photoelectron transitions of the PVP-CuCl₂ catalyst were observed at 932.10 eV with a shoulder peak at 934.01 eV. The difference of the Cu_{2p_{3/2}} binding energies between PVP-CuCl₂ and CuCl₂ is 2.91 and 1.0 eV, respectively, therefore the XPS spectra of the PVP-CuCl₂ catalyst indicates that a strong electronic modification of Cu(II) takes place during the complexation. These results suggest that coordination bonds may have occurred between N, O atom and metal atom, and thus Cu(II) are immobilized on the polymer.

It is known that IR is useful for detecting the molecular interaction between two species. The structure of the PVP-CuCl₂ catalyst has been investigated by using FTIR. As shown in Fig. 1, the peak of C=O bond in PVP becomes obviously asymmetric on adding CuCl₂, indicating that the interaction between PVP and Cu(II) in the PVP-CuCl₂ complex is very strong. FTIR spectra of both PVP and PVP-CuCl₂ catalyst show characteristic bands at 3000 and 3400 cm⁻¹ originating from PVP (not shown). The carbonyl band

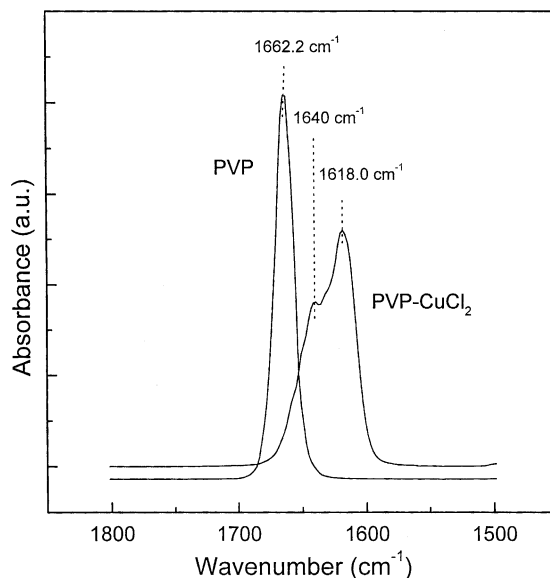


Fig. 1. FTIR spectra of: (a) PVP and (b) PVP-CuCl₂ (N/Cu = 2/1) complexes.

of PVP appearing at 1662.2 cm⁻¹ is due to the stretching band of amide carbonyl group in PVP, whereas it shifts to 1618 cm⁻¹ with a well-resolved shoulder at 1640 cm⁻¹ in PVP-CuCl₂ complexes. Compared to that of PVP, these bands were shifted to much lower wavenumbers indicating the existence of ligand interaction between amide carbonyl moiety and Cu(II) species. Wuepper and Popov [26] have previously reported that a red shift of carbonyl band was observed in the IR spectrum of 2-pyrrolidone in the presence of alkali metal ions. They concluded that the band shift was due to the interaction between the carbonyl oxygen of 2-pyrrolidone and the metal ions. Therefore, the present IR data provide evidence the presence of a strong ligand interaction between inorganic Cu(II) species and the polymeric PVP ligands in PVP-CuCl₂ catalyst system. Coupled with the XPS data, the difference in the spectra between PVP and PVP-CuCl₂ are due to the presence of strong donor–acceptor interaction between O, N atom in PVP and Cu(II) ions. Two possible schematic molecular structures of the PVP-CuCl₂ catalyst system are proposed as in Scheme 2. It is shown in Scheme 2 that structure (a) is formed by the formation of coordination linkage between the oxygen and nitrogen atoms of amide carbonyl groups and the Cu(II) ion, while the structure

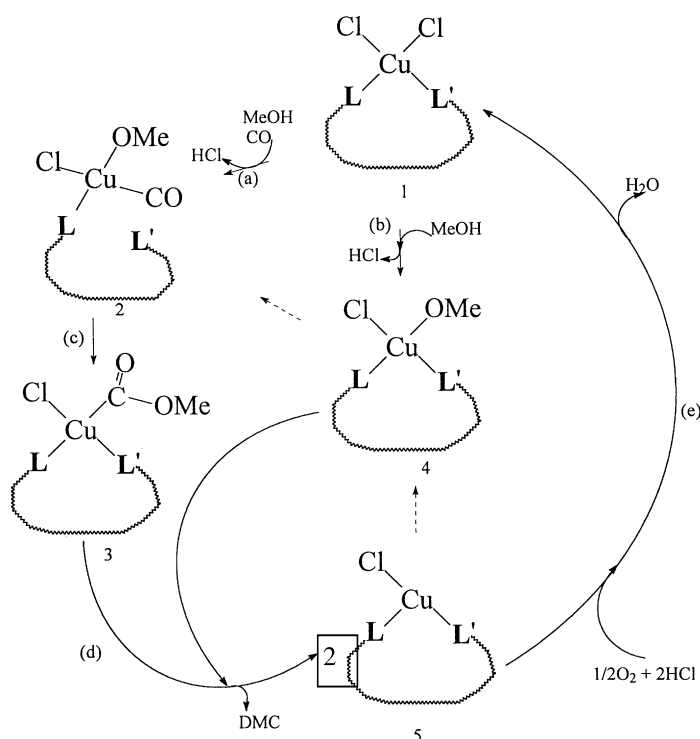
(b) involves simultaneously the ligand interactions between Cu(II) ion and two oxygen atoms from the carbonyl groups of two neighboring amide ligands.

3.4. Reaction mechanism

In the conventional Wacker-type homogeneous redox system consisting of Pd and Cu, the Cu–Pd couple bridged by $-Cl-$ species has known to be highly reactive for the redox process of Cu(II)/Cu(I) and Pd(0)/Pd(II) at the same time. Thus, it is understandable that the randomly supported, as well as separated Pd and Cu species on Y zeolite have shown a low reactivity in the gas-phase reaction. In our case, the particularly high activity of the PVP-CuCl₂ catalytic system may be attributed to the presence of a strong coordination between the amide ligands pendant to the backbone of the polymer chain in PVP and the Cu(II) ions in CuCl₂. It is known that the unique structure of PVP possesses the highly polarized amide groups which make the carbonyl group in the amide moieties

particularly active in formation of ligands to transition metallic cations by providing excess electrons. Thus, the polymeric ligand of PVP containing the highly polarized amide groups can establish coordinate linkage between the carbonyl moiety and Cu(II) species, which were suggested to facilitate the Cu(II)/Cu(I) redox processes by providing electrons through the carbonyl oxygen atoms.

It has been well established that two-electron transfer is necessary for the synthesis of one DMC molecule. Previously, Romano et al. [27] proposed that two types of reaction intermediates is directly involved in the process of DMC synthesis with Cu(I)Cl catalytic system and the active species have been suggested to be CuCl(OCH₃). Based on the previous mechanistic studies and present experimental results, a possible reaction mechanism for the PVP-CuCl₂ catalyzed synthesis of DMC is proposed as in Scheme 3. Two types of Cu(II)/(I) redox systems for the polymeric PVP-Cu(II)Cl₂ catalytic system have been considered. As shown in Scheme 3, the intermediate



Scheme 3. Proposed reaction mechanism for PVP-CuCl₂ complex catalyzed oxidative carbonylation of methanol to dimethyl carbonate. (L = O, L' = O or N).

1 undergoes the ligand exchange reaction (a) to produce **2** and the subsequent CO insertion gives the formation of **3** via path (c). On the other hand, another molecule of **1** is converted into **4** by ligand exchange with MeO^- through path (b). Obviously, it is important that the two Cu(II) species **3** and **4** in Scheme 3 have a contact in the reaction process, which allows the production of one DMC molecule and two molecules of Cu(I) complexes. The starting Cu(II) compound **1** is regenerated by the oxidation of **5** with O_2 through step (e).

It is, therefore, understandable that the presence of polymeric PVP, forming a complex with CuCl_2 , could increase the electron density of the central Cu(II) cations so that the complex catalyst favors the formation of reaction intermediates and the insertion of carbon monoxide. Recently, several heterogeneous polymer-immobilized CuCl_2 complexes have been reported to exhibit comparable activity and selectivity to that of CuCl_2 in the liquid-phase synthesis of DMC [14–18]. These heterogenized CuCl_2 catalysts containing pyridine ligands are industrially attractive since they are non-corrosive in the reaction. It is concluded that the nitrogen-containing pyridine groups with π -conjugation in the polymer chain serve as electron donating ligands which facilitate the redox of the Cu(II)-polymer complex in the catalytic reaction. Compared to the present homogeneous PVP-bound CuCl_2 catalyst, the relatively low catalytic activities of the heterogeneous polypyridine- CuCl_2 catalytic systems can be explained by considering the additional fact that Cu atoms are randomly supported and separated which greatly reduces the opportunity for the two intermediates **3** and **4** to interact.

We have demonstrated that the present homogeneous polymer-bound monometallic PVP- CuCl_2 catalyst is promising excellent catalytic system for the oxidative carbonylation of methanol with methanol, carbon monoxide and O_2 in liquid-phase. It is shown that the variable of reaction conditions including the catalyst composition, temperature and reaction time have a significant influence on the DMC synthesis reaction. However, to gain a more detailed understanding toward the nature of the active species of the PVP- CuCl_2 system and the modification effect of polymeric PVP ligands on activities of the Cu(II) ions in the oxidative carbonylation of methanol,

various other spectroscopic characterizations needed to be further carried out.

4. Conclusion

In summary, a new efficient homogeneous polymer-bound monometallic PVP- CuCl_2 catalytic system has been studied for the catalytic oxidative carbonylation of methanol to DMC. It is shown that the incorporation of amide ligands containing PVP polymers can remarkably improve the catalytic properties of CuCl_2 catalyst for the oxidative carbonylation of methanol to DMC. The polymer-bound PVP- CuCl_2 catalytic system provides a good conversion and selectivity for the oxidative carbonylation of methanol and CO to DMC under optimal conditions. The combined XPS and FTIR data provide evidence that the complexation of the carbonyl groups of the amide ligands in polymeric PVP with CuCl_2 results in the formation of a coordinated copper species which are directly responsible for the high catalytic activity and selectivity of the PVP- CuCl_2 catalyst system for DMC synthesis. Other experiments are in progress to gain further understanding of this particular oxidative carbonylation catalyst system.

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