

A NEW HOMOGENEOUS ELECTROCATALYST FOR ELECTROCHEMICAL CARBONYLATION OF METHANOL TO DIMETHYL CARBONATE

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Electrosynthesis of dimethyl carbonate (DMC) from methanol and carbon monoxide using an $\text{Cu}(\text{phen})\text{Cl}_2$ catalyst was achieved at room temperature and atmospheric pressure. The catalytic activity of the ligand 1,10-phenanthroline (phen) and the catalytic system were analyzed. The IR characterization results for the complex catalyst showed that copper ions were coordinated by nitrogen atoms of phen. In addition, the effects of the influencing factors, such as reaction time (t), reaction temperature (T) and the surface area of the working electrode (S_{WE}) were studied.

Keywords: electro-synthesis; DMC; homogeneous catalyst.

INTRODUCTION

Dimethyl carbonate (DMC) is viewed as an environmentally benign intermediate because of its negligible eco-toxicity and its versatile chemical applications.¹⁻³ DMC has been proposed as a replacement for phosgene, dimethyl sulfate, chloromethane and other toxic/carcinogenic substances as methylating reagents, carbonylating reagents and ester interchange reagents.^{3,4} In addition, DMC are employed as electrolytes in energy materials⁵ and are widely used as fuel additives and polar solvents.^{6,7} Furthermore, DMC is also a very important synthetic intermediate and building block in the current chemical industry.² Thus, from the above point of view, DMC have received increasing attentions in each area.

There are several commercial processes for the production of DMC, such as phosgenation,⁸ oxidative carbonylation of methanol,⁹ transesterification,¹⁰ direct synthesis from carbon dioxide and methanol¹¹ and urea methanolysis method.¹² Among these methods, oxidative carbonylation of methanol has been considered as one of most popular phosgene-free routes for DMC synthesis. However, the oxidative carbonylation of methanol suffers from harsh reaction conditions, potential explosion of carbon monoxide (CO), and a large number of by-products. An electrochemical synthesis method based on our previous investigations^{13,14} has proposed for producing dimethyl carbonate under safer and milder conditions. Electrocatalysis is potentially useful for redox reaction, which electrons transfer as oxidant instead of O_2 . Oxidation potential can be easily controlled, and can inhibit the formation of H_2O .¹⁵

Among the catalysts involved in this electrocatalytic reaction, previous studies from other researchers suggest that noble metals (such as Pd,¹⁶ Rh,¹⁷ Au¹⁸) exhibited outstanding electrocatalytic activity. However, the high cost of the requisite noble metals has been inhibited their large-scale commercial applications. Although the non-noble metals generally have the advantages of low cost, but simple transition metal salts showed poor electrocatalytic activity. To address this problem, nitrogen-chelating bidentate ligands were introduced and coordinated with the transition metal salts.

We have demonstrated that $\text{Cu}(\text{bipy})\text{Cl}_2$ (bipy = 2,2'-bipyridine) was very active for the electroactivated carbonylation to DMC.¹³ Recently, we have replaced the ligand and succeeded in the electrochemical oxidative carbonylation of methanol to DMC at room

temperature and atmospheric pressure in the two-compartment electrolytic cell.

In this work, 1,10-phenanthroline (phen) was chosen to be the N-donor ligand, which can coordinate with cupric chloride. Phen is a classical chelating bidentate N-donor ligand, possess a rigid planar, hydrophobic, electron-deficient heteroaromatic system.¹⁹ Phen behaves as a weak base in aqueous solution and displays superior coordination ability for transition metal cations.²⁰ Therefore, compared to the bipy, phen possesses a stronger and more entropically favoured metal binding. In other words, phen coordinating with Cu^{2+} ions can form more rapidly and a higher stability than bipy. To the best of our knowledge, the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$, has not been reported for the electrosynthesis of DMC.

EXPERIMENTAL

Reagents and instruments

All reagents and solvents were of analytical grade and used without further purification. Electrochemical analyzer (CHI 660C, Shanghai Chenhua Instrument Co., Ltd., PR China), gas chromatograph (GC-17A with flame ionization detector and 30 m \times 0.25 mm capillary column, Shimadzu), Fourier transform infrared spectroscopy (Nexus 670, Nicolet), two-compartment electrolytic cell (self-fabricated) were used in the experiment.

Electrosynthesis using two-compartment cell

The electrosynthesis of DMC from methanol and carbon monoxide was carried out in the self-fabricated two-compartment electrolytic cell made of polytetrafluoroethylene (PTFE). The anodic compartment was equipped with gas inlet and outlet as well as reference ($\text{Ag}/\text{Ag}_2\text{O}$) and working electrodes (carbon rod). The cathodic compartment was equipped with counter electrode (copper wire). Anode and cathode compartments were divided by anion exchange membrane. Each compartment had a volume of 20 cm^3 . More details about the structure of the electrolytic cell and working conditions are described in our previous work.^{13,14}

The main reaction steps are as follows: First, CH_3OH (10 mL) and supporting electrolyte KOH (0.1 mol L^{-1} , 0.0562 g) was added into the anode and cathode compartments. The CO was then bubbled into the anode compartment using a tubule for 10 min to remove the

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oxygen (The CO passed through the drying tower with CaCl_2 at first, and then into a buffer bottle with methanol, and was finally bubbled into the anode compartment). The same as a reaction reagent, CO was bubbled into the anode compartment in the whole electrolysis process. Lastly, anhydrous copper chloride (0.07 mol L^{-1} , 0.0941 g) and phen (0.07 mol L^{-1} , 0.1261 g) were added into the anode compartment to begin the electrolysis, which was carried out under 0.3 V potentiostatic condition at 298 K and atmospheric pressure. The surface area of the working electrode was 188.40 mm^2 . The potentiostatic condition was provided by the electrochemical analyzer.

Purification and analysis of products

After the electro-synthesis reaction proceeded 2 h, the anolyte was placed into a round bottom flask, and underwent a simple distillation to remove the solid ions. The distillate was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Analysis of the catalytic activity of phen

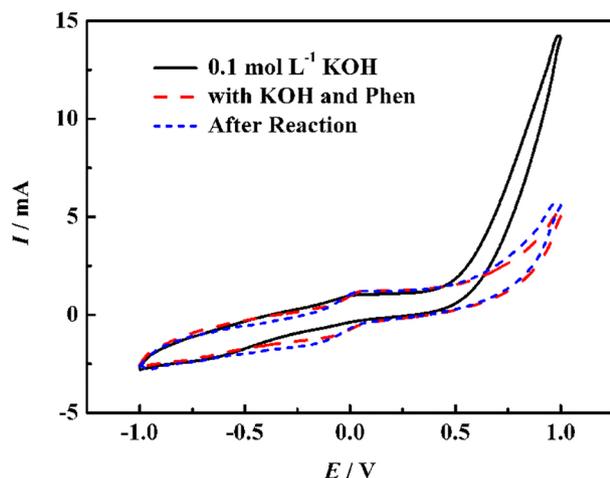


Figure 1. Cyclic voltammograms of the electro-synthesis system with phen as the catalyst (Voltage scan rate = 100 mV s^{-1} ; electrolyte, KOH (0.1 mol L^{-1})/ CH_3OH)

In order to verify if phen has catalytic performance on the electro-synthesis of DMC, the following experiment was conducted. When other reagents were all added to the electrolytic cell, except CuCl_2 , the CV spectra of the system are shown in Figure 1. From Figure 1, no obvious oxidation or reduction peaks were observed during the whole 2 h procedure. The characteristic curves of CV mean that there is no redox reaction occurred in the system before and after the reaction under the potential of -1.0 V to $+1.0 \text{ V}$, and the electro-synthesis system during the reaction almost had no change. These phenomena indicate that phen does not have catalytic activity on the electro-synthesis of DMC, which is corresponding to the result of the GC analysis of the distilled anolyte after reaction. The fact further indicates that phen played a single role as the common ligand in the electrocatalyst.

Analysis of the catalytic system

After the analysis of the catalytic activity of phen, the catalytic system was studied, as shown in Figure 2, the cyclic voltammetry of the electro-synthesis system at different stages was conducted. In Figure 2(A), when the electrolyte KOH and phen were added to the anolyte, the CV curve of the electro-synthesis system had no obvious

oxidation or reduction peaks, however, when continue to add CuCl_2 to the anolyte, the CV curve of the electro-synthesis system had a pair of obvious redox peaks, at the end of reaction, the redox peaks changed to two pairs.

Based on the characters of the CV curves in Figure 2(A), we deduced when CuCl_2 was added to the anolyte, phen and CuCl_2 formed the complex $\text{Cu}(\text{phen})\text{Cl}_2$ *in situ*, which has catalytic activity towards the electro-synthesis of DMC. The GC data showed that a certain amount of DMC were synthesized in the anolyte. Moreover, we deduced the complex catalyst was destroyed after the electro-synthesis reaction, so the redox peaks of the CV curve of the electro-synthesis system changed to two pairs.

The following experiments were designed to confirm if the deduction obtained above was reasonable. From Figure 2(B) we can see it clearly that when CuCl_2 was added, the CV curve of the electro-synthesis system had two pairs of redox peaks, and when phen was added, the redox peaks of the CV curve of the electro-synthesis system changed to one pair, however, when the electro-synthesis reaction was ended 2 h later, the redox peaks of the CV curve of the electro-synthesis system changed to two pairs again.

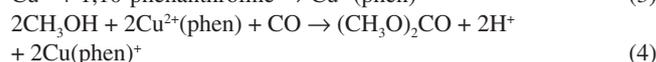
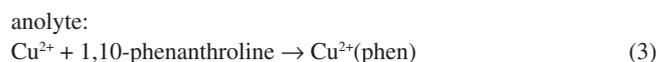
The characters of the CV curves in Figure 2(B) indicated that the appearance of the two pairs of redox peaks was attributed to CuCl_2 , when phen was added, CuCl_2 and phen occurred a process of coordination, formed the complex $\text{Cu}(\text{phen})\text{Cl}_2$ *in situ*, so the redox peaks of the CV curve of the electro-synthesis system changed to one pair. The electro-synthesis system after reaction reflected the electro-chemical properties of CuCl_2 , it meant that as the electro-synthesis reaction progress, the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$ was destroyed, the reason for this destruction most likely is that phen was degraded gradually as the electro-synthesis reaction progress, so the CuCl_2 was released from the complex $\text{Cu}(\text{phen})\text{Cl}_2$.

In Figure 2(C), as the electro-synthesis reaction proceeded, the current intensity of the electro-synthesis system increased at first, then decreased. The reason for this phenomenon is that as the formation of the complex $\text{Cu}(\text{phen})\text{Cl}_2$ *in situ*, the reaction rate of the electro-synthesis system increased at the beginning of the reaction, then with the electro-synthesis reaction proceeded, the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$ was destroyed gradually, therefore, the reaction rate of the $\text{Cu}(\text{phen})\text{Cl}_2$ catalyzed electro-synthesis system decreased in the reaction process.

From Figure 2(D), we can see when the equal amount of phen were added to the electro-synthesis system after reaction, the CV curve of the electro-synthesis system similar to before. It indicated that when phen was added after reaction, the catalyst activity regenerated. In other words, when phen was added after reaction, the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$ formed again in the electro-synthesis system. Thus it is concluded that the destruction of the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$ was proved due to the degradation of phen in the reaction process.

Mechanism of the electro-synthesis processes

The electrochemical reaction equations of the experiment were estimated as follows:



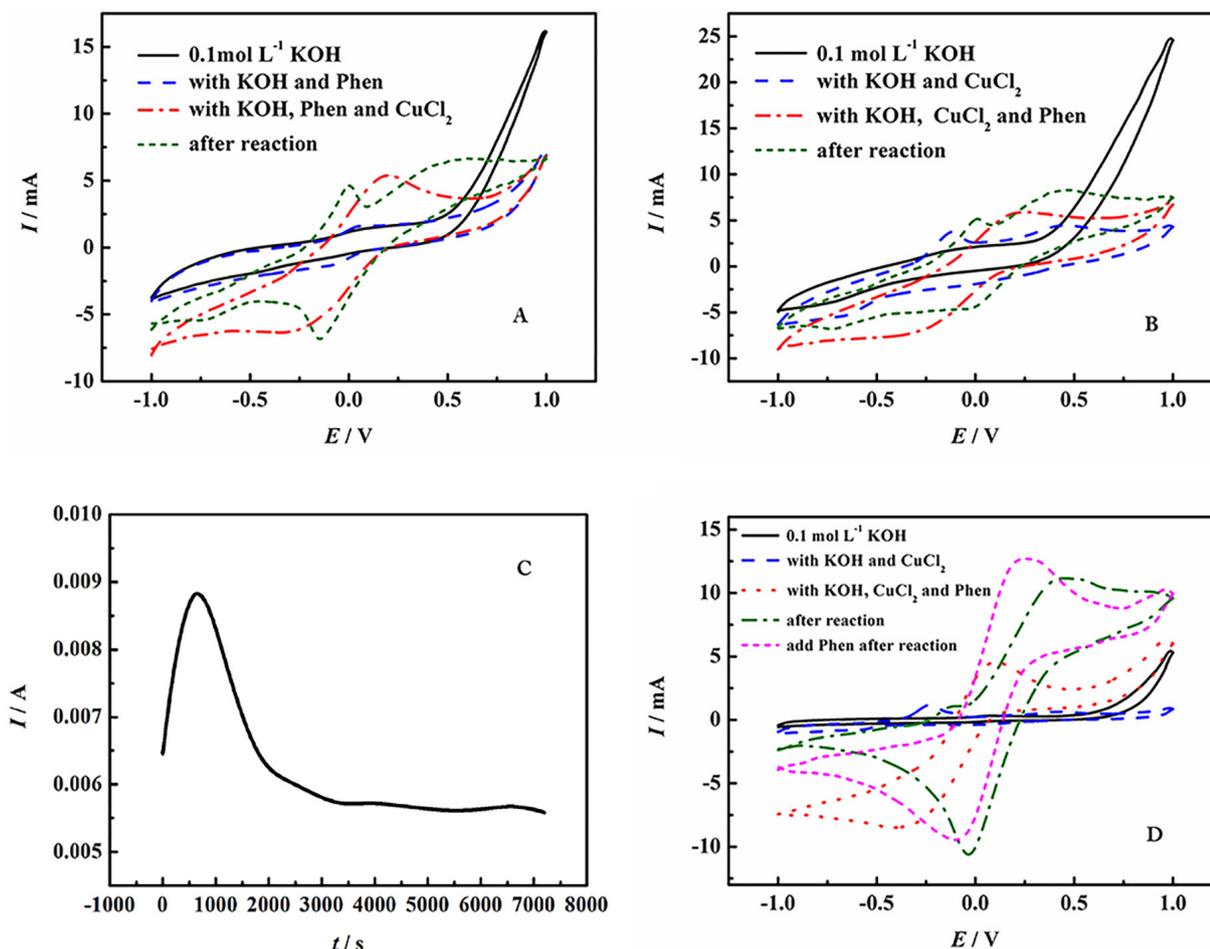


Figure 2. (A, B) Cyclic voltammograms of the electro-synthesis system at different stages; (C) Current-Time Curve of the whole process of $\text{Cu}(\text{phen})\text{Cl}_2$ catalyzed electro-synthesis of DMC from CH_3OH and CO ; (D) Cyclic voltammograms of the electro-synthesis system add phen after reaction. General conditions: CH_3OH (10 mL) + KOH (0.1 mol L^{-1}) + CuCl_2 (0.07 mol L^{-1}) + phen (0.07 mol L^{-1}), $T = 298 \text{ K}$, $P = 1 \text{ atm}$. CE: copper wire, WE: carbon rod, RE: $\text{Ag}/\text{Ag}_2\text{O}$

The mechanism of the electro-synthesis processes were presented in Figure 3. For the electro-synthesis of one DMC molecule, at least two-electron transfer is necessary. In alkaline medium, the protons could be abstracted from methanol to form CH_3O^- anions. In addition, the dissociative chemisorption of CH_3OH on metal surfaces by the O–H bond breaking to produce methoxyl intermediates is widely accepted as a common view. From the above point of view, The methoxy group was first attaches to the metal center of the electrocatalyst by nucleophilic attack. The interaction and reaction between methanol and the $\text{Cu}(\text{II})$ complex led to the Cl^- anions removal from the metal center. The insertion of CO into the $\text{Cu}-\text{O}$ bond is the rate-determining step of the whole reactions. The next stage is divided into two different ways. One route is accompanied with the production of DMC, a chloride ion bridged dinuclear Cu^{II} complex was generated simultaneously, which might be inactive for the electrocatalytic reactions. Once DMC generated, the other route is the generation of the $\text{Cu}^{\text{I}}(\text{phen})\text{Cl}$, and then it was oxidized back to $\text{Cu}(\text{phen})\text{Cl}_2$ at the anode. In this mechanism, the electron transfer process is very important. Coupled with this, due to the existence of the electron or redundant oxygen, Cu^{2+} ions of the metal complex might be disproportionate into Cu^+ and low-spin Cu^{3+} ions. As a result, a part of $\text{Cu}^{\text{II}}(\text{phen})\text{Cl}_2$ could be disproportionate into $\text{Cu}^{\text{I}}(\text{phen})\text{Cl}$ and $\text{Cu}^{\text{III}}(\text{phen})\text{Cl}_3$. To a certain extent, this process may promote the electro-synthesis reaction.

Characterization of the complex catalyst $\text{Cu}(\text{phen})\text{Cl}_2$

The FTIR spectrum of the ligand phen shown in Figure 4(1)

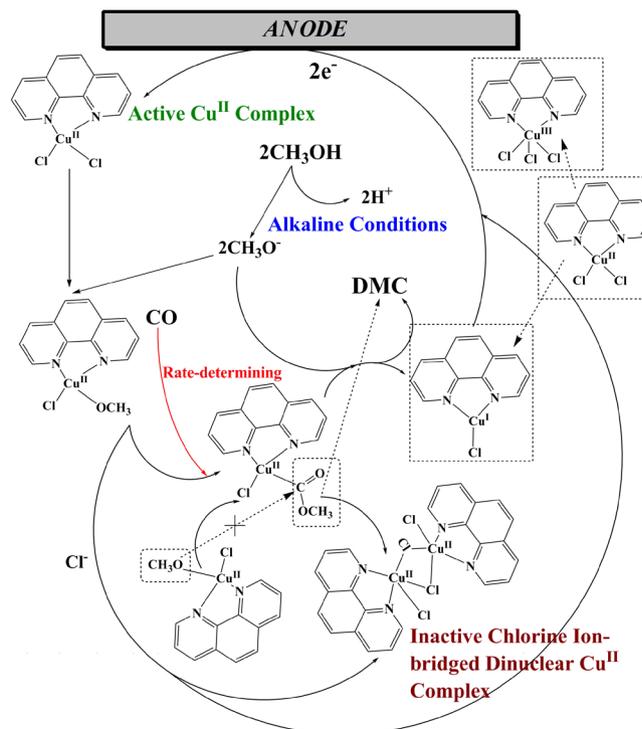


Figure 3. Schematic illustration of possible reaction mechanism for the electro-synthesis of DMC catalyzed by $\text{Cu}(\text{phen})\text{Cl}_2$

contains four characteristic peaks: the stretching vibration peaks of C=N and C=C double bonds appear at 1638 cm^{-1} and 1583 cm^{-1} for phen, the skeleton vibration peak of ligand phen appears at 1560 cm^{-1} , and the out-plane bending vibration peak of C-H bond appears at 735 cm^{-1} . The FTIR spectrum of the synthesized complex is presented in Figure 4(2). Compared with the spectrum of the ligand phen (Figure 4(1)), the stretching vibration peaks of C=N ($\nu_{\text{C=N}}$, 1638 cm^{-1}) and C=C ($\nu_{\text{C=C}}$, 1583 cm^{-1}) of phenyl ring in ligand phen have shifted to 1626 and 1587 cm^{-1} , respectively. The skeleton vibration peak of ligand phen shifts from 1560 to 1516 cm^{-1} , and the out-plane bending vibration peak of C-H bond also shifts from 735 cm^{-1} in the phen to 719 cm^{-1} in the complex.

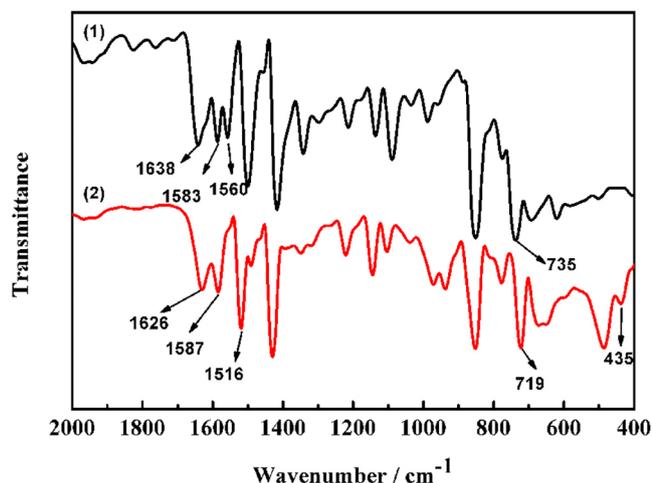


Figure 4. FT-IR spectra of 1,10-phenanthroline (1) and the Cu(phen)Cl_2 complex (2)

The stretching vibration absorption band of the C=C double bond blue-shifted and the other absorption bands red-shifted, suggesting that the nitrogen atoms of the heterocyclic ligand phen coordinate with the Cu^{2+} ion. Meanwhile, the absorption band at 435 cm^{-1} in the complex is assigned to the stretching vibration of Cu-N bond and thus further demonstrates that the nitrogen atoms in the ligand take part in coordination.

Study on the influencing factors

In this part, we discussed the influencing factors such as reaction time, reaction temperature and the surface area of the working electrode.

The effects of reaction time (t) on the Cu(phen)Cl_2 catalyzed electrosynthesis of DMC from CH_3OH and CO were studied, as shown in Figure 5(A). With the increase of reaction time, the content of DMC in anode electrolyte increased first, and then decreased. At $t = 2\text{ h}$, the content of DMC reached a maximum. This is because that after starting the electrosynthesis reaction, under the action of catalyst Cu(phen)Cl_2 , reactants in the system gradually converted into products, therefore, when $t \leq 2\text{ h}$, the content of DMC in anode electrolyte increased with the increase of reaction time. But, as the reaction progress, on the one hand, the catalytic activity decreased with the degradation of phen in the complex catalyst Cu(phen)Cl_2 ; on the other hand, the synthesis reaction is reversible, when $t > 2\text{ h}$, the DMC formation rate is lower than the decomposition rate, therefore, when $t > 2\text{ h}$, the content of DMC in anode electrolyte decreased with the increase of reaction time.

The effects of reaction temperature (T) on the Cu(phen)Cl_2 catalyzed electrosynthesis of DMC from CH_3OH and CO were studied,

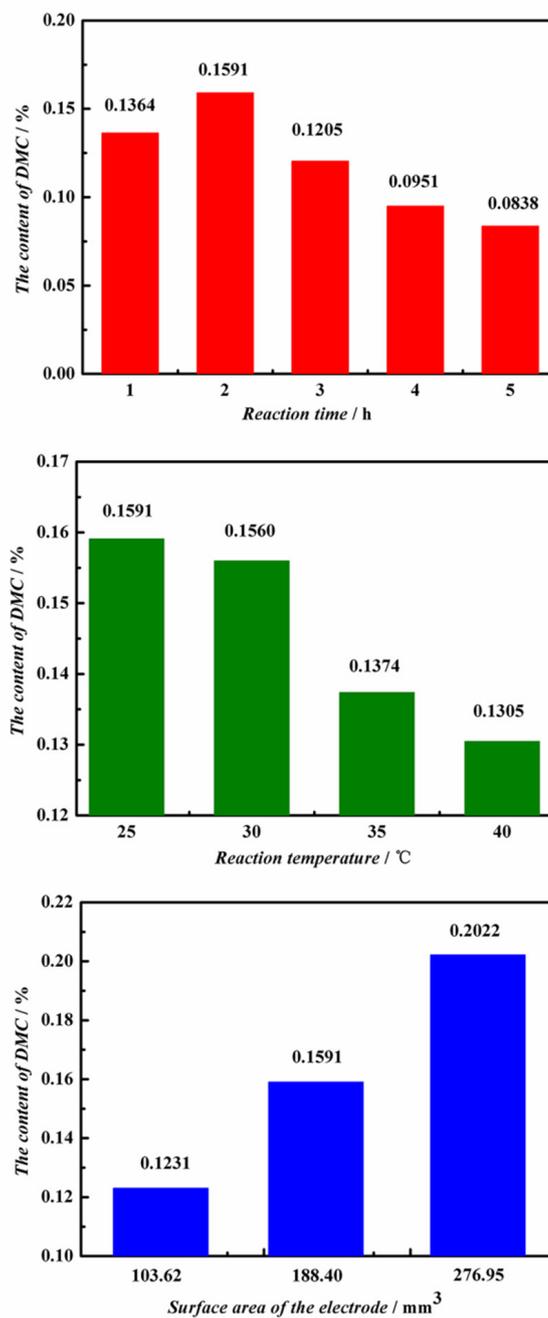


Figure 5. Effect of reaction time (A), effect of reaction temperature (B) and effect of the surface area of working electrode (C) on the Cu(phen)Cl_2 catalyzed electrosynthesis of DMC from CH_3OH and CO

as shown in Figure 5(B). With the increase of reaction temperature, the content of DMC in the anode electrolyte decreased drastically. At $T = 298\text{ K}$, the content of DMC in anode electrolyte was highest. It is because that with the increase of reaction temperature, CO as one of the reactants, its solubility decreased, thus limiting the reaction. Besides, the reaction of synthesis of DMC from CH_3OH and CO is exothermic, elevated temperatures are not conducive to the formation of DMC, to the contrary, to promote the inverse of the reaction, namely, to promote the decomposition of the DMC. Due to the above two reasons, therefore, with the increase of reaction temperature, the content of DMC in the anode electrolyte decreased drastically. That is, when $T > 298\text{ K}$, the content of DMC in the anode electrolyte were all lower than that of 298 K .

Figure 5(C) showed the effects of the surface area of the working

electrode (S_{WE}) on the Cu(phen)Cl₂ catalyzed electrosynthesis of DMC from CH₃OH and CO. From Figure 5(C) we can see, with the increase of the surface area of the working electrode (surface covered by solution took part in the reaction), the content of DMC in the anode electrolyte showed an almost linear upward trend. It means that the larger the surface area of the working electrode, the more beneficial to the synthesis of DMC. In electrolysis under controlled potential with a larger surface area of the working electrode a larger current will be observed, and consequently an increase of Coulombs/unit time which will cause the formation of a larger amount of DMC/unit time. Thus, the more beneficial to the synthesis of DMC.

CONCLUSIONS

The electrosynthesis of dimethyl carbonate from methanol and carbon monoxide over Cu(phen)Cl₂ catalyst can be achieved at atmospheric pressure and room temperature. Phen only as a ligand in the electrosynthesis reaction, and itself has no catalytic activity towards the reaction. In the electrosynthesis system, phen coordinated with CuCl₂ *in situ*, formed the complex Cu(phen)Cl₂, which is active towards the electrosynthesis of DMC from methanol and carbon monoxide at room temperature and atmospheric pressure. However, the ligand was degraded during the process of the electrosynthesis reaction and therefore that result in the destruction of the complex, which made the catalytic activity decreased.

The IR characterization results of the complex catalyst showed that copper ions were coordinated by nitrogen atoms of phen. Based on the optimized condition: $t = 2$ h, $T = 298$ K, $S_{WE} = 276.95$ mm², the content of DMC was 0.2022%, the amount of DMC was 0.4991 mmol.

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