The catalytic performance and corrosion inhibition of CuCl/Schiff base system in homogeneous oxidative carbonylation of methanol

Wanling Mo, Hui Xiong, Tao Li, Xiaochuan Guo, Guangxing Li *

Department of Chemistry, Huazhong University of Science & Technology, Wuhan 430074, PR China

Abstract

A homogeneous catalytic system, CuCl/Schiff base, was studied in the synthesis of dimethyl carbonate (DMC) by oxidative carbonylation of methanol. It was found that among a number of Schiff bases studied, 1,10-phenanthroline (phen) was the most effective promoter in terms of both the catalytic activity and the corrosion inhibition. The catalytic performance of CuCl was enhanced dramatically and the corrosion of the reaction system was effectively inhibited when phen was used as a ligand. At a reaction condition with a catalyst concentration of 0.2 mol/L, $n_{Cu}/n_{phen} = 2:3$, temperature = 120 °C, time = 2 h, $P = 2.4$ MPa and $P_{CO}/P_{O_2} = 2 : 1$, the conversion of methanol is 23.7%, the selectivity to dimethyl carbonate is 98.3% and the TON is 14.4. The catalytic activity increased by about 270% and the lifetime increased by greater than threefold relative to the CuCl catalyst without addition of phen. The corrosion rates to the HC276 and HC686 stainless steels by the CuCl/phen catalyst are 0.0282 and 0.0071 mg/h. In comparison with CuCl catalyst, the inhibition efficiencies (IE) on HC276 and HC686 stainless steel are 95.4% and 98.5%, respectively, under the same reaction conditions. Scanning electron microscopy (SEM) showed that the pitting corrosion was not observed on the HC686 stainless steel surface after adding phen. The adsorption layer of phen on the surface of the corrosion specimen can prevent the pitting corrosion of the material.
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1. Introduction

Dimethyl carbonate (DMC) is an environment friendly building block for versatile chemical applications. It has been used as a non-toxic carbonylating and methylating agent to substitute for phosgene and dimethyl sulfate—two toxic and corrosive chemicals that industry has been trying to phase out [1–3]. The production of dimethyl carbonate has received increasing attention. Up to now, there are three main routes for the production of DMC [4–6]. (1) The phosgene method by which DMC is produced by reaction of highly toxic COCl$_2$ with methanol. (2) The transesterification of ethylene or propylene carbonate with methanol, with which glycol as a by-product is produced. The productivities and "atom economy" of this scheme are low and the industry profit is strongly tied to the ethylene glycol or propylene glycol market. (3) The oxidative carbonylation of methanol with carbon monoxide and oxygen. This process matches best the principles of "green chemistry", which has the lowest impact on human health and environment.

The oxidative carbonylation process, based on homogeneous reaction, using copper chloride as catalyst was first developed by ENIchem in 1983. But this catalytic system has two primary drawbacks. Cuprous chloride is sparingly soluble in methanol. As a result, the reactants cannot react with the catalyst efficiently to form active intermediate, and the per pass conversion must be kept low in order to avoid water reaction with the copper salts [4,5]. Furthermore, copper chloride is highly corrosive to metallic vessels due to the existence of Cl⁻ and the redox reaction of Cu [7]. For many years, in order to overcome these drawbacks various catalytic systems have been studied. Many kinds of base additives for use as promoters or cosolvents (such as amines and pyridines (Py)), as well as immobilized copper salt catalysts on inorganic or organic solid materials have been investigated [8–14].

Recently, Sato et al. [12] immobilized CuCl$_2$ on various polymers containing N-donor ligand aromatic support

* Corresponding author. Tel.: +86 27 87543732; fax: +86 27 87544532.
  E-mail address: ligxabc@public.wh.hb.cn (G. Li).

[12–14]. The supported catalysts can decrease the corrosion obviously, but the conversion of methanol is very low (<3%) and there is still hydrolysis of DMC to CO_2 and MeOH, which makes the yield and selectivity low. Sundermeyer and co-workers studied the influence of monodentate N-donor ligands on the copper catalyzed oxidative carbonylation of methanol to DMC [15]. Though the catalyst, copper coordinated with 1-methylimidazole (NMI), can increase the conversion of methanol, trace amount of NMI may evaporate and contaminate the product. N−N bidentate ligands have exhibited highly promoting effect for the reaction of oxidative carbonylation [16,17]. In view of literature, catalytic activity and corrosion are hard to compromise. Hence, the goal of the present work is to enhance the catalytic activity and minimize the corrosion of the catalyst to the reactor materials simultaneously. We focus on the influence of various N-donor ligands coordinating with copper on the catalytic reactivity in the reaction of oxidative carbonylation. To the best of our knowledge, the homogeneous catalytic system, CuCl/phen, has not been reported for the synthesis of DMC.

2. Experiment

Catalytic oxidative carbonylation of methanol was performed in a 0.25 L stainless steel autoclave lined with Teflon, equipped with a magnetic stirrer. All reagents were used as received without further purification. In a typical experiment, methanol, an N-donor ligand and the cuprous chloride were loaded into the autoclave. The autoclave was purged three times with CO and then pressurized to 2.4 MPa with CO and O_2 ($P_{CO}/P_{O_2} = 2 : 1$) at room temperature. When the temperature went up to 363 K, the magnetic stirrer was turned on and then the temperature was held at 393 K. During the reaction, the mixture of CO and O_2 was added to maintain the total pressure at 2.4 MPa. After the reaction, the reactor was cooled down to room temperature and depressurized. The liquid product was collected and distilled at atmosphere pressure. The main by-products were water and methyl acetate in the reaction. The concentrations of DMC and methyl acetate were determined by gas chromatography (GC) using an FID detector.

CH_3OH conversion and DMC selectivity were calculated by the following equations:

$$CH_3OH \text{ conversion} = 2 \times \frac{n_{DMC} + n_b}{n_{MeOH}} \times 100\%$$

$$DMC \text{ selectivity} = \frac{n_{DMC}}{n_{DMC} + n_b} \times 100\%$$

where n_{DMC} is the molar amounts of the DMC, n_{MeOH} is the molar amounts of the methanol and n_b is the molar amounts of the methyl acetate.

The rate of the absorption of gases was measured by recording the pressure of autoclave and the reaction time. The original pressure of autoclave was 2.4 MPa (at room temperature, $P_{CO}/P_{O_2} = 2 : 1$). The catalyst lifetime was estimated according to the description above procedure. At the end of each run, the gas was vented first and the liquid phase was evaporated. Then

fresh methanol, CO and O_2 were added. During the reaction the rate of corrosion, in mg/h, was measured by method of weight loss. Test pieces (about 20 mm × 10 mm × 3 mm) of Hastelloy HC276 (Cr 15%, Mo 16%, Fe 6%, W 4%, C ≤ 0.01%, Ni base) and HC686 (Cr 21%, Mo 16%, Fe ≤ 1%, W 3.7%, C ≤ 0.01%, Ni base) (from Special Metals Corporation, USA) were introduced into the autoclave using a special sample cage. The corrosion data were obtained at 393 K after reaction for 72 h under a pressure of 2.4 MPa. The inhibition efficiency (IE) was calculated using the following equation:

$$IE = \frac{\text{corrosion rate of CuCl} - (\text{corrosion rate of CuCl/Schiff base})}{\text{corrosion rate of CuCl}}$$

The contents of Cu and Cl in fresh and deactivated catalysts were measured by using X-ray fluorescence (EAGLE III of America EDAX Inc.). The surface morphology of HC686 corrosion pieces was measured using a scanning electron microscopy (SEM) (Quanta 200 of Philip FEI Inc.).

3. Results and discussion

3.1. Effects of N-donor ligands on the catalytic activity

The role of the N-donor ligands in catalytic performance of CuCl for synthesis of DMC has been investigated by testing the catalytic activity (Table 1 and Fig. 1) and the rate of absorption of gases (Fig. 2).

Results in Table 1 show that among imidazole (IM) and its substitutes, CuCl/NMI has the highest catalytic activity, corresponding to a methanol conversion of 15.4%. However, the CuCl/imidazole has the lowest activity, corresponding to a lowest methanol conversion of 4.8%. This means that imidazole does not increase the methanol conversion at the reaction conditions. Among the pyridine and its substitutes, CuCl/2-aminopyridine has the highest activity, with a methanol conversion of 13.2%. In addition, no any other by-product was detected. Among the N−N bidentate ligands system, the CuCl/phen catalyst shows the highest activity, with a methanol conversion of 23.7% and the yield of DMC of 23.3%. This conversion is the highest one among all the N-donor ligands systems investigated. Compared with CuCl catalyst without any additives, the catalytic activity is enhanced with addition of various N-donor ligands; especially in the case of phenanthroline (phen), the catalytic activity is enhanced about 3.7 times.

Generally, N-donor heterocyclic ring ligands are both σ-donating and π-accepting. The more the σ-donor ability is, the more the π-accepting capacity is [18]. Different substituents on the heterocyclic ring affect its basicity, or σ-donor ability. The relationship between the σ-donor ability of the N-donor ligands, which can be expressed by their pK_a values [19], and their catalytic performance is shown in Fig. 1. The relationship of pK_a and the conversion of methanol indicate that the promoting abilities of the N-donor ligands are related to both the σ-donor ability and the molecular structure of ligands.

Under the reaction conditions shown in Table 1, the catalytic activity of CuCl/IM is very low. The reason may be that imida-

Table 1
Effects of N-donor ligands on the catalytic activities

No.	Ligand	$C_{Ligands}$ (mol/L)	X_{MeOH} (%)	S_{DMC} (%)	TON	pK_a [19–21]
1	No	–	6.4	96.4	3.9	–
2	Imidazole	0.6	4.8	>99.9	3.0	6.95
3	2-Methylimidazole	0.6	11.5	98.4	7.0	7.86
4	1,2-Dimethylimidazole	0.6	12.8	98.7	7.8	8.2
5	1-Methylimidazole	0.6	15.4	98.8	9.0	7.06
6	Pyridine	0.6	8.8	99.4	5.4	5.17
7	4-Dimethylaminopyridine	0.6	9.8	99.1	6.0	9.70
8	2-Methylpyridine	0.6	12.0	99.0	7.4	5.96
9	2-Aminopyridine	0.6	13.2	>99.9	8.2	6.71
10	5-Nitro-phen	0.3	6.5	>99.9	4.0	2.80
11	5-Amino-phen	0.3	16.5	99.0	10.2	5.23
12	2,2′-Bipyridine	0.3	17.9	97.2	10.8	4.35
13	phen	0.3	23.7	98.3	14.4	4.86

Reaction conditions: methanol 80 mL, CuCl 200 mmol/L, $P_{CO}/P_{O_2} = 2 : 1$, 2.4 MPa, 120 °C, 2 h, stirring speed 1000 rpm; $C_{Ligands}$: the molar concentration of N-donor ligands; X_{MeOH}: the conversion of methanol; S_{DMC}: the selectivity to dimethyl carbonate.
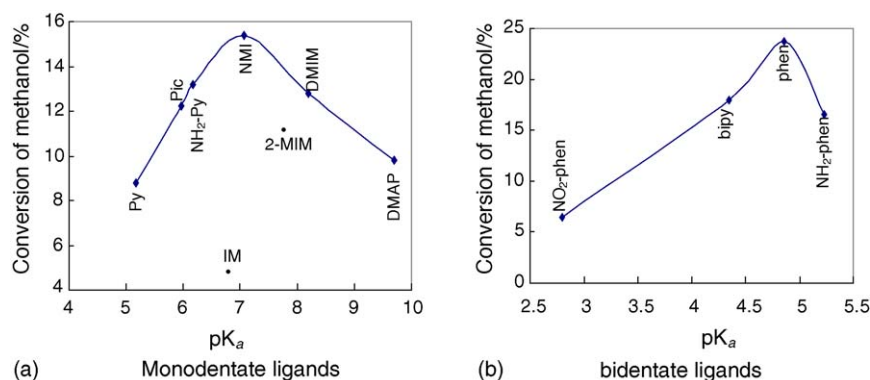

Fig. 1. Relationship between pK_a of the N-donor ligand and conversion of methanol. Py: pyridine; Pic: 2-methylpyridine; NH₂-Py: 2-aminopyridine; DMAP: 4-dimethylaminopyridine; NMI: 1-methylimidazole; DMIM: 1,2-dimethylimidazole; IM: imidazole; 2-MIM: 2-methylimidazole; NO₂-phen: 5-nitro-phen; bipy: 2,2′-bipyridine; NH₂-phen: 5-amino-phen.
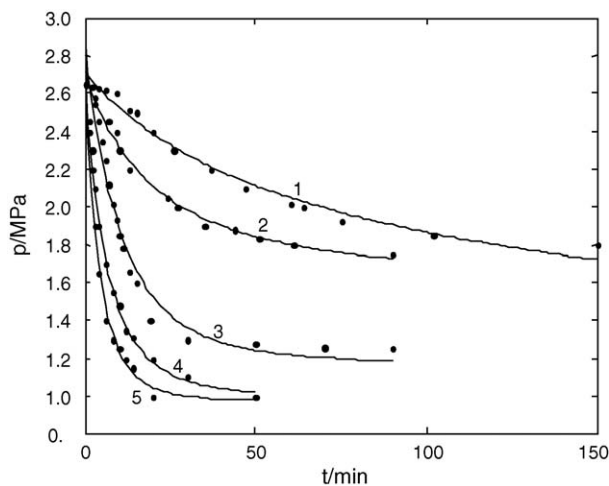

Fig. 2. The variation of pressure with time for different catalysts. (1) CuCl; (2) CuCl/Py; (3) CuCl/NIM; (4) CuCl/bipy; (5) CuCl/phen. *Reaction conditions*: methanol 80 mL, CuCl 200 mmol/L, 120 °C, 2 h, stirring speed 1000 rpm.

zole molecules interact with each other by hydrogen bonding, forming a long chain structure [22] that can prevent the reactants, CH_3O^- and CO, from coordinating with Cu(I) to form the active intermediate species. This may also be true for the CuCl/2-methylimidazole (2-MIM) catalyst.

In N–N bidentate ligands, the promoting effect of phen is higher than that of bipyridine (bipy). This may be due to the stronger basicity, chelating power and rigidity of phen [23]. In homogeneous carbonylation of nitrobenzene catalyzed by the $[Pd(chel)_2][PF_6]_2$ catalyst, Mestronic et al. found that the conversion (in 2 h) of nitrobenzene rose from 14.5% to 72% when changing the promoter from bipy to phen. For the oxidative carbonylation of phenol, the chelating ligands produce similar promoting effects. When bipy and phen were used as promoters, the productivity of diphenyl carbonate (DPC) was 14 and 16 mol DPC/mol Pd h, respectively [17]. On the other hand, for phen and its substitutes the decreasing trend of the catalytic activity in the sequence of phen > 5-amino-phen (NH₂-phen) > 5-nitro-phen (NO₂-phen) may be related to the σ-donor ability and hydrogen bonding between the molecules. The hydrogen bonding between molecules of 5-NH₂-phen may not be beneficial to the coordination of CO and CH_3O^- with
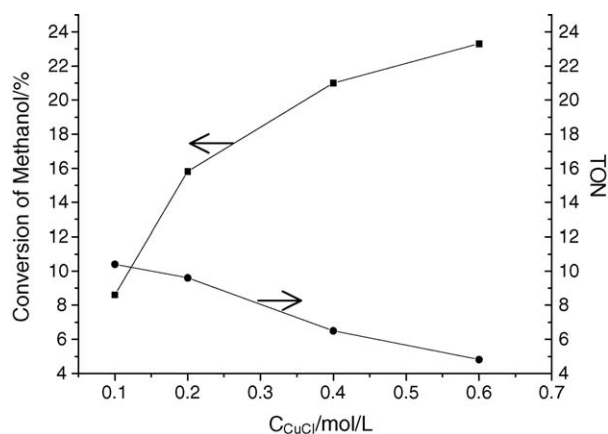
Fig. 3. Effect of the concentration of the catalyst on the catalytic performance. *Reaction conditions*: methanol 80 mL, $P_{CO}/P_{O_2} = 2 : 1$, 2.4 MPa, 120 °C, 2 h, stirring speed 1000 rpm.

Table 2
Effect of the phen concentration on the catalytic performance

C_{phen} (mol/L)	n_{Cu}/n_{phen}	X_{MeOH} (%)	S_{DMC} (%)	TON
0.05	4:1	9.6	97.9	5.8
0.2	1:1	20.5	98.4	12.5
0.3	1:1.5	23.7	98.3	14.4
0.4	1:2	16.8	99.2	10.3
0.5	1:2.5	5.4	99.0	3.3

Reaction conditions: methanol 80 mL, CuCl 200 mmol/L, $P_{CO}/P_{O_2} = 2 : 1$, 2.4 MPa, 120 °C, 2 h, stirring speed 1000 rpm.

the Cu(I) complex. This makes its promoting ability lower than phen. The σ-donor ability of 5-nitro-phen is weaker than phen, due to the electron withdrawing effect of the −NO$_2$ group. This is a disadvantage to the coordination of CO and CH$_3$O$^-$ with Cu(I) complex.

According to the mechanism of oxidative carbonylation in the presence of CuCl catalyst [5,11,13,15], CO forms a monocarbonyl complex with cuprous chloride, COCuCl, which interacts with copper methoxide to form carbomethoxide intermediate (Cu−CO−OCH$_3$)$^+$. The main factor that affects the rate of reaction is the rates of copper methoxide formation and the CO insertion. As described above, different N-donor ligands affect the coordination of CO and CH$_3$O$^-$ with Cu(I) complex. So the rate of the absorption of gases varied remarkably with different N-donor ligands.

The results in Fig. 2 show that the rates of copper methoxide formation and the CO insertion are very slow when CuCl is used as the catalyst. In contrast, the rates become very high when CuCl/Schiff base is used as the catalyst, especially when CuCl/phen is used. Yamamoto and co-workers [14,24] found that the π-conjugated character of the N-donor ligands played an important role in accelerating the Cu(II)/Cu(I) redox cycle, which is consistent with our experiments.

3.2. Effect of the concentration of CuCl/phen catalyst

Influences of the concentrations of CuCl/phen catalyst on the conversion and TON are presented in Fig. 3.

When the molar ratio of CuCl/phen is kept at 2:1, the conversion of methanol increases from 8.6% to 23.3% when the

concentration of CuCl increases from 0.1 to 0.6 mol/L and that of the TON decreases from 10.4 to 4.8.

On the other hand, if the concentration of CuCl is kept at 0.2 mol/L, the conversion of methanol and TON increases first and then decreases when the molar ratio of CuCl/phen changes from 4:1 to 1:2.5. There is no significant change in the selectivity of DMC as seen from Table 2.

The phen can coordinate with copper to form mono-chelate ring or bis-chelate ring complexes (Scheme 1). When the concentration of phen is too low, copper in the reaction system cannot coordinate with phen effectively to form enough active intermediates to catalyze the oxidative carbonylation. In contrast, when the concentration of phen is too high, copper coordinates with the N-donor ligand strongly and forms bis-chelate ring complex, making the ligand hard to leave to provide coordination vacancy for CO and CH$_3$O$^-$. Taking into account of the conversion of methanol and TON of dimethyl carbonate, the optimum concentration of CuCl is about 0.2 mol/L with phen 0.3 mol/L.

3.3. Lifetime of the catalyst

A catalyst with reasonably long lifetime is critical to its application in industry. The durability of CuCl/phen and CuCl catalysts were tested in a batch system described above and the results are shown in Fig. 4. It can be seen that the selectivity of DMC is kept at about 99.5% and the catalytic activity showed no significant change after 16 runs for the CuCl/phen catalyst; however, the catalytic activity of the CuCl catalyst decayed rapidly after 5 runs, and the conversion of methanol dropped markedly from 9.6% to only 3.2%.

Table 3 shows that the molar ratio of Cl/Cu is 1.02 and 0.82 for the fresh and deactivated catalyst, respectively. The loss of chlorine is about 20%. At the same time, no phen (<10 ppm) in the products is detected by UV–vis spectrophotometer. These results indicate that the loss of chlorine accounts primarily for the deactivation of the catalyst. Thus, chloride ion is an essential component of the catalysts. It was assumed that chloride acts
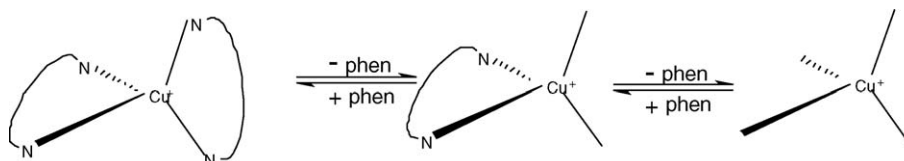
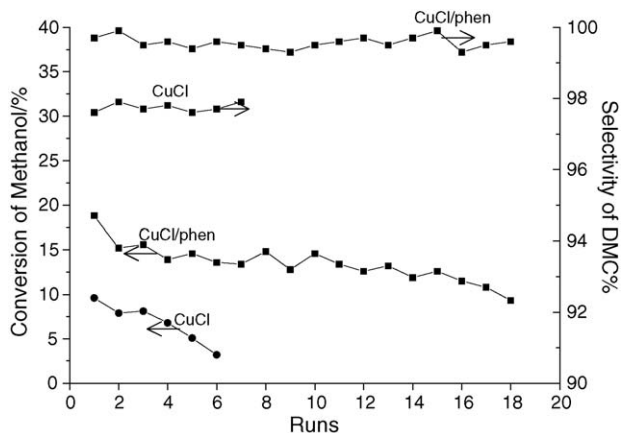Scheme 1. Coordination of phen to Cu$^+$ ion.

Fig. 4. Lifetime of CuCl/phen and CuCl catalysts. *Reaction conditions*: methanol 100 mL, CuCl 300 mmol/L, phen 150 mmol/L, $P_{CO}/P_{O_2} = 2:1$, 2.4 MPa, 120 °C, 3 h, stirring speed 1000 rpm.

Table 3
The composition of chlorine and copper of the fresh and the deactivated catalysts

Elements[a]	Fresh catalyst (at%)	Deactivated catalyst (at%)
Cl	50.48	45.08
Cu	49.52	54.95
Cl/Cu	1.02	0.82

[a] The data in table are obtained by XRF, which can only detect the elements after Na in the periodic table, therefore, the elements of C, O, H and N in the catalysts cannot be detected.

as three-electron donor ligand for the formation of the mixed valent Cu(I,II)-chloro-and-methoxo-bridged clusters that may be involved in the cycle for the synthesis of DMC [15]. Eyring and co-workers suggested that in the oxidative carbonylation of ethanol to diethyl carbonate, chloride ion may serve as a bridge between copper ion and one of the reactants, which should increase the kinetics of electron transfer [25].

Romano et al. [5] discussed the deactivation mechanisms for CuCl catalyst. Copper salts are unstable when excess amount of water builds up, resulting in the formation of a variety of copper hydroxy chloride phases, $Cu(Cl)_x(OH)_y \cdot nH_2O$, none of which are effective catalysts in the production of DMC. The chlorine-to-copper ratio in the reactor also affects the rate and

Table 4
Corrosion inhibition of phen promoters

Catalyst	Corrosion rate (mg/h)		IE (%)	
	HC276[a]	HC686[a]	HC276	HC686
CuCl	0.6198	0.4774		
CuCl₂[b]	8.3			
PVP-CuCl₂[b]	0.9		89.2	
PBPy-CuCl₂[b]	0.6		92.8	
PPy-CuCl₂[c]	0.3		96.4	
CuCl/phen	0.0282	0.0071	95.4	98.5

Reaction conditions: methanol 100 mL, CuCl 200 mmol/L, phen 200 mmol/L, $P_{CO}/P_{O_2} = 2:1$, 2.4 MPa, 120 °C, 72 h, stirring speed 600 rpm.
[a] HC276 (stainless steel): Standard No. B575 (ASTM); HC686 (stainless steel): Standard No. B575-97 (ASTM).
[b] Reported in Ref. [12].
[c] Reported in Ref. [14].

selectivity of the DMC formation. The optimum chlorine-to-copper ratio is close to 1.0 [5]. By adding phen, the lifetime of CuCl/phen catalyst is extended. This indicates that phen can enhance the stability of the CuCl/phen catalyst and avoid the catalyst deactivating.

3.4. Corrosion inhibition

The corrosion rates of the CuCl and CuCl/phen catalytic systems have been determined and the results are presented in Table 4.

Results in Table 4 clearly indicate that the corroding effect to HC276 and HC686 is very severe, and the pitting corrosion is observed on the metal surface in CuCl and CuCl₂ catalytic systems. With addition of phen, the corrosion is effectively inhibited and the pitting corrosion is not observed, as revealed by a scanning electron microscopy image (Fig. 5). It has been reported that severe corrosion caused by halogen ion can be considerably reduced by immobilizing of the catalyst. Based on this consideration, Sato et al. [12,14] immobilized CuCl₂ on N-donor polymer supports and greatly reduced the corrosion performance of halogen. However, the corrosion rate of their polymer supported CuCl₂ catalysts is 10–30 times that of our CuCl/phen catalyst. Somasundaran and co-workers found that the severe
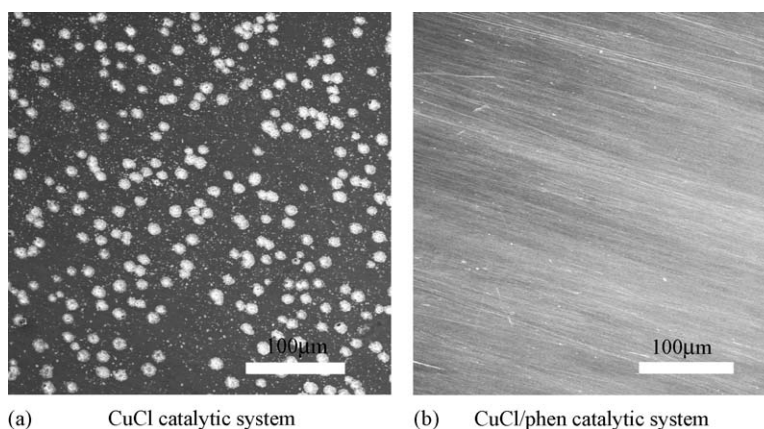

(a)   CuCl catalytic system

(b)   CuCl/phen catalytic system

Fig. 5. SEM photographs of corrosion specimen under *reaction conditions*.

corroding effect of halogen ions can be greatly reduced by adsorbing organic molecules on metal surfaces [26,27]. Our present work suggests that HC276 and HC686 themselves alone are inadequate for being used as the reactor material when CuCl is used as the catalyst. Nevertheless, when phen is added to the catalytic system, the corrosion of the CuCl/phen catalyst to the HC276 and HC686 steels become very light, and hence they can be used as the reactor materials. The reduction in the corrosion may be due to the adsorption of phen on the metal surface, preventing the pitting corrosion of the material.

4. Conclusion

In this work, we have demonstrated that Schiff base promoters with different σ-donor abilities and molecular structures affect the catalytic performance of CuCl differently for oxidative carbonylation of methanol to DMC. Among the catalysts of CuCl/Schiff base studied, the catalyst of CuCl/phen exhibited high catalytic activity, long lifetime and excellent corrosion resistance.

Acknowledgments

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