

Catalytic Properties of Cu Complexes in Oxidative Carbonylation of Methanol

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Keywords: Dimethyl carbonate; Cu(II)-1,10-phenanthroline complex; Methanol; Oxidative carbonylation.

Abstract. The thermostability of Cu(II)-1,10-phenanthroline complexes was studied by the thermogravimetric analysis, and their catalytic properties were evaluated in oxidative carbonylation of methanol to dimethyl carbonate. It was found that the copper coordination environments and the thermostability of the complexes played important roles in their catalytic activities. Cu(1,10-phenanthroline)Cl₂ exhibited the highest activity due to the lowest steric hindrance, the highest coordination probability and the highest thermal stability. With the addition of CuCl, the activity of Cu(1,10-phenanthroline)Cl₂ could be further improved and the turnover number of dimethyl carbonate increased from 39.0 to 46.9 mol_{DMC}/mol_{Cu}.

Introduction

Dimethyl carbonate (DMC) is a green chemical, and can be used as carbonylation reagent or methylation reagent to substitute for phosgene or dimethyl sulfate, respectively. Among several methods available for phosgene-free synthesis of DMC[1], the one-step oxidative carbonylation of methanol with CO and O₂ is the most perspective route.

CuCl is known as a traditional catalyst in the oxidative carbonylation of methanol[2]. But this system has some disadvantages, such as the low solubility in methanol, high corrosiveness to metallic vessels due to the existence of Cl⁻, and so on.

The N-donor ligand is added to overcome these shortcomings. Xiong et al reported that the activity and the corrosiveness of CuCl could be improved effectively with the addition of N-methyl imidazole (NMI)[3]. When N-butylpyridinium tetrafluoroborate was used as the reaction media, the solubility of CuCl in methanol was enhanced from 0.44 to 2.2 g/100 g, and the quantity of DMC was also raised from 2.3 to 4.6 g/(L_{cat}·h)[4]. Considering that the solubility of CuCl in methanol is very low, CuCl₂ is chosen as the copper source. Raab et al has found that NMI could improve the activity of CuCl₂ greatly and reduce the corrosion of the autoclave[5].

Although the N-ligand is introduced to promote CuCl_x-catalyzed (x = 1 or 2) synthesis of DMC, there is no direct evidence for the promotion behavior of the ligand because of the difficulties to determine the structure and ingredient of the copper complexes, which are formed in situ in the oxidative carbonylation of methanol. Fundamentally, the central copper ion configuration is the key to understand the nature of the Cu-catalyzed DMC formation.

Recently our research group found that Cu(phen)Cl₂ (phen = 1,10-phenanthroline) showed the higher catalytic activity for the DMC formation than the mixture of CuCl₂ and phen[6]. In order to reveal the reason, we focus on the researches of relationship between the structures and the catalytic activity. In this paper, Cu(phen)Cl₂, [Cu(phen)₂Cl]Cl·H₂O and [Cu(phen)₃]Cl₂·7H₂O were prepared, and their catalytic properties were tested in the oxidative carbonylation of methanol to DMC.

Experimental

Chemical reagents. All reagents were purchased from local manufactures and used without further purification. Cu(phen)Cl₂, [Cu(phen)₂Cl]Cl·H₂O and [Cu(phen)₃]Cl₂·7H₂O were synthesized according to the literatures [1].

Catalyst characterization. Thermogravimetric analysis (TGA) was carried out on a TGA Q50 analyzer at a heating rate of 10 °C/min from room temperature to 800°C.

The CO-TPR analysis of Cu(phen)Cl₂ was carried out on a Micro Auto Chem II 2920 at a heating rate of 10°C/min from 45 to 300°C.

Reaction procedure and product analysis. The oxidative carbonylation of methanol with CO and O₂ was carried out in a 250 mL stainless steel autoclave. 40 mL of methanol and 0.011 mol/L of the catalyst were loaded into the autoclave. The autoclave was purged three times with O₂, and then pressurized to 4.0 MPa with CO and O₂ ($P_{CO}/P_{O_2} = 19:1$) at room temperature. The system was heated to 120 °C and kept for 4h. After the reaction, the reactor was cooled to room temperature. The reaction mixture was analyzed by a GC-2014 (Shimadzu) equipped with a Rtx-50 capillary column (30 m × 0.32 mm × 0.25 μm) and flame ionization detector.

Results and Discussion

Effect of the thermal stability of the complex on the catalytic activity. The reaction temperature is usually over 110 °C in the oxidative carbonylation of methanol to DMC, so the thermostability of Cu(II) complexes is a key. They were characterized by the thermogravimetric analysis.

It can be seen from Figure 1(a) that the weight loss of Cu(phen)Cl₂ appears at 290 °C. The loss is 57.5% in the 290 ~ 720 °C range, close to the 57.1% weight content of phen in Cu(phen)Cl₂, so the temperature range should be ascribed to the decomposition of phen. This result implies that Cu(phen)Cl₂ can meet the temperature requirement of the carbonylation reaction. [Cu(phen)₂Cl]Cl exhibits the 3.4% weight loss (seeing Figure 1(b)) from 80 to 180 °C, implying that there is one crystal water in the complex. When the temperature is above 220 °C, the loss may be attributed to its decomposition, so its thermal stability is also favorable to the oxidative carbonylation. In the TG patterns shown in Figure 1(c), the weight loss of 22.0 % below 104 °C probably rises from the removal of crystal waters in [Cu(phen)₃]Cl₂. The continuous weight loss should stem from its thermal degradation above 104 °C. Thus the thermal stability of [Cu(phen)₃]Cl₂ is unfavorable to the oxidative carbonylation.

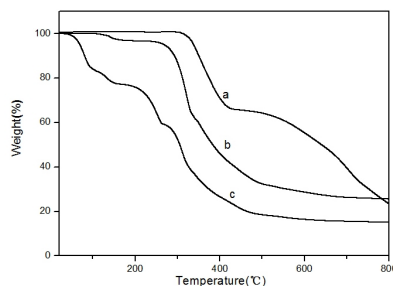


Fig. 1. TG patterns of Cu(phen)Cl₂ (a), [Cu(phen)₂Cl]Cl·H₂O (b), [Cu(phen)₃]Cl₂·7H₂O (c).

Catalytic performances of Cu complexes. In order to compare with the activity of Cu complexes, CuCl₂ and the equimolar mixture of phen and CuCl₂ were used to catalyze the oxidative carbonylation of methanol with CO and O₂. The results are listed in Table 1. The turnover number (TON) was 16.3 mol_{DMC}/mol_{Cu} with CuCl₂ used as the catalyst, and the selectivity of DMC was 97.4%. As a sole by-product, dimethoxymethane (DMM) was detected with the 2.6% selectivity. When the equimolar amount of phen was added, TON and the selectivity of DMC increased to 22.9 mol_{DMC}/mol_{Cu} and 97.8%, respectively. This suggests that the σ-π coordination bond between phen and Cu(II) can improve the catalytic activity of CuCl₂. However, when Cu(phen)Cl₂ was used to catalyze the oxidative carbonylation of methanol, it is interesting to note that TON and the selectivity of DMC were improved further, up to 39.0 mol_{DMC}/mol_{Cu} and 98.3%, respectively. In order to explain the activity difference, the pre-treatment time of the mixture, referring to the mixed time of phen and CuCl₂ before the reaction started, was investigated. As shown in Table 1, TON and the selectivity of DMC increased with the rise of the pre-treatment time, and were gradually close to 39.0 mol_{DMC}/mol_{Cu} and 98.3%. The results show that the reaction time is very important for the synthesis

of Cu(phen)Cl₂ from phen and CuCl₂, and the conditions of the oxidative carbonylation are unfavorable to the in-situ synthesis of Cu(phen)Cl₂.

Table 1 Effect of different catalysts on oxidative carbonylation of methanol

Catalyst	S _{DMC} (%)	S _{DMM} (%)	TON (mol _{DMC} / mol _{Cu})	Pre-treatment time (min)
CuCl ₂	97.4	2.6	16.3	
*CuCl ₂ +phen	97.8	2.2	22.9	5
Cu(phen)Cl ₂	98.3	1.7	39.0	
*CuCl ₂ +phen	98.0	2.0	26.1	10
*CuCl ₂ +phen	98.1	1.9	35.2	20
[Cu(phen) ₃]Cl ₂ ·7H ₂ O	>99.9	0	1.5	
[Cu(phen) ₂]ClCl·H ₂ O	99.7	0.3	4.7	

*The molar ratio of phen to Cu(II) is 1:1. Reaction Conditions: V_{MeOH} 50 mL, C_{Cu} = 0.011 mol/L, 120 °C, 4 MPa, 4 h.

Detoni et al reported that the Cu complex with two phen ([Cu(phen)₂Cl]Cl) showed the higher activity than Cu(phen)Cl₂ and [Cu(phen)₃]Cl₂ in the oxidation of cyclohexane[7], so the effect of the structures of Cu complexes on the activity was also tested. TON on [Cu(phen)₃]Cl₂·7H₂O was only 1.5 mol_{DMC}/mol_{Cu} (seeing Table 1), where the copper coordination environment is hexacoordination. Combined with Table 1 and Figure 1, we think that the low activity is probably caused by the following factors: firstly, the steric hindrance around Cu(II) is very large due to the formation of six Cu–N bonds, thus the coordination of the complex with methanol or CO is inhibited, and the thermal stability of [Cu(phen)₃]Cl₂·7H₂O is also lowered because of the mutual repulsion from three phen rings (seeing Table 2); secondly, the saturation of the first coordination sphere reduces the probability of raw material molecules to be coordinated with Cu(II); thirdly, the catalytic performance of the complex is relevant to the σ-π coordination bond between phen and Cu, while the initial decomposition temperature of [Cu(phen)₃]Cl₂·7H₂O is only 104 °C, implying that the σ-π coordination bond is destroyed easily, so the catalytic activity decreases. With the decrease of the phen number, [Cu(phen)₂Cl]Cl·H₂O, in which the copper center is pentacoordinated, has the low steric hindrance, the unsaturation of the first coordination sphere and labile positions occupied by Cl⁻, so the coordination probability is enhanced between [Cu(phen)₂Cl]Cl·H₂O and methanol or CO. At the same time, its initial decomposition temperature increases to 220 °C, indicating that the influence of the reaction temperature on the σ-π coordination bond decreases. TON increased to 4.7 mol_{DMC}/mol_{Cu}. With the further decrease of the phen number, Cu(phen)Cl₂, in which copper is tetraordinated[1], has the lowest steric hindrance and the highest coordination probability stemming from the rise of the unsaturation of the first coordination sphere and labile positions occupied by Cl⁻, and the 290 °C initial decomposing temperature is also the highest, thus TON arrived to 39.0 mol_{DMC}/mol_{Cu}. However, the high activity of the Cu complex can also accelerate the rate of the side reaction, so the selectivity of DMC decreased gradually in the following order: Cu(phen)Cl₂ < [Cu(phen)₂Cl]Cl·H₂O < [Cu(phen)₃]Cl₂·7H₂O.

Table 2 The initial decomposition temperature and TON of the complexes

Catalyst	Initial decomposition temperature / (°C)	TON/ (mol _{DMC} /mol _{Cu})
[Cu(phen) ₃]Cl ₂ ·7H ₂ O	104	1.5
[Cu(phen) ₂ Cl]Cl·H ₂ O	220	4.7
Cu(phen)Cl ₂	290	39.0

Effect of the addition of CuCl. In the oxidative carbonylation of methanol, a mixed valence Cu(I, II)-ligand-bridged cluster is a key intermediate to form copper methoxycarbonyl species[6], so it is very necessary for the coexistence of Cu(II) and Cu(I). Cu(phen)Cl₂ was characterized by the CO-TPR analysis and the pattern is shown in Figure 2. No peaks were detected in the 50~300 °C range. The result demonstrates that it is impossible for the in-situ reduction of Cu(phen)Cl₂ to Cu(phen)Cl under the reaction conditions. Therefore, the addition of CuCl may improve the activity of Cu(phen)Cl₂.

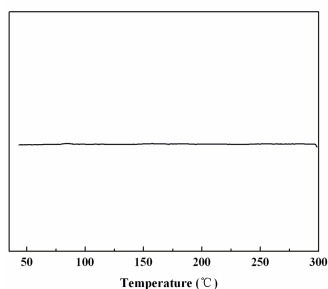


Fig. 2 CO-TPR pattern of Cu(phen)Cl₂ reaction

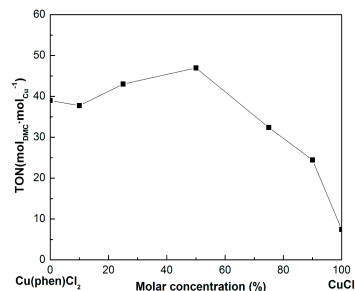


Fig. 3 Effect of the molar ratio of Cu(phen)Cl₂ to CuCl on the reaction

As shown in Figure 3, TON increased gradually with the addition of CuCl. The result confirms the addition of CuCl is in favor of the synthesis of DMC. When the molar ratio of Cu(phen)Cl₂ to CuCl is 1:1, the mixture catalyst revealed the highest activity. TON was up to 46.9 mol_{DMC}/mol_{Cu}, more than 39.0 mol_{DMC}/mol_{Cu} over Cu(phen)Cl₂. Above 1:1, TON decreases due to the poor solubility of CuCl in methanol. Consequently, the optimal molar ratio of Cu(phen)Cl₂ to CuCl is 1:1.

Conclusions

Three Cu(II)-1,10-phenanthroline complexes and the equimolar mixture of phen and CuCl₂ were used as catalysts for the oxidative carbonylation of methanol to DMC. It was found that the coordination environments and the thermal stability of complexes would influence the steric and electronic properties of the catalytic centers and the catalytic behaviors. Cu(phen)Cl₂ exhibited the highest activity because of the lowest steric hindrance, the highest coordination probability and the highest thermal stability. TON reached to 39.0 mol_{DMC}/mol_{Cu} with the 98.3% selectivity under the standard batch reaction conditions ([Cu(II)] = 0.011 mol · L⁻¹, 0.2 MPa O₂, 3.8 MPa CO, 120 °C and 4 h). With the addition of CuCl, the TON value of DMC was enhanced further to 46.9 mol_{DMC}/mol_{Cu}.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21276201).

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