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Oxidative Carbonylation of Methanol to Dimethyl Carbonate Over Cu(II)–1,10-Phenanthroline Bromide Complexes ☆

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ABSTRACT

In order to develop the catalysts with low corrosiveness for the oxidative carbonylation of methanol to dimethyl carbonate (DMC), $CuBr_2$ was selected as the metal source to prepare Cu coordination compounds, $Cu(phen)Br_2$, $[Cu(phen)_2Br]Br$ and $[Cu(phen)_3]Br_2$ (phen = 1,10-phenanthroline). These complexes were characterized by thermogravimetric analysis and temperature-programmed reduction. Their catalytic performances were investigated. It was found that the metal coordination environments and thermal stability of the complexes played an important role in their catalytic activities. $Cu(phen)Br_2$ exhibited the highest activity due to the lowest steric hindrance, the most positions occupied by the bromide ions and the highest thermal stability. The turnover number was up to 47.6 DMC mol·(Cu mol)$^{-1}$ with selectivity of 92.8% under conditions of 120 °C, ratio of partial pressure of CO to O_2 of 19:1 (below the explosion limit of CO) and catalyst concentration of 0.011 mol·L^{-1}. Furthermore, a plausible reaction mechanism was suggested on the basis of the experimental data.

1. Introduction

As an environmentally benign chemical, dimethyl carbonate (DMC) can be used as the carbonylation reagent and the methylation reagent to replace highly toxic phosgene or dimethyl sulfate [1-4]. DMC has been drawing attention as a safe solvent and an additive in lithium-ion batteries. DMC can also be used potentially as a fuel additive to replace methyl *tert*-butyl ether (MTBE) due to its high oxygen content, good blending octane, rapid biodegradability and low toxicity [5,6].

Among several phosgene-free methods for the synthesis of DMC, the oxidative carbonylation of methanol is the most perspective route, in which CuCl is used as a catalyst [7-9]. However, this catalytic system suffers from some disadvantages, such as the losing activity due to the decomposition of CuCl, the corrosiveness caused by the chlorine ions and the redox reaction of copper.

In order to overcome these drawbacks, the influence of *N*-ligand on CuCl was studied [10–14]. It was found that 1,10-phenanthroline (Phen) was the most effective promoter in terms of the catalytic activity and the corrosion inhibition. Xiong and co-workers reported that Phen and *N*-methylimidazole (NMI) exhibited a synergic effect on the catalytic activity of CuCl [15]. When *N*-butylpyridinium tetrafluoroborate ($[BPy]BF_4$) was used as reaction media, the solubility of CuCl in methanol increased from about 0.0044 g·g^{-1} to 0.022 g·g^{-1}, and the conversion of methanol and the selectivity of DMC were enhanced from 9.0% and 97.3% to 17.8% and 97.8%, respectively [16]. Considering the low solubility of CuCl in methanol, $CuCl_2$ is selected to catalyze the oxidative carbonylation of methanol as well. Raab and co-workers found that the addition of NMI could enhance the catalytic activity of $CuCl_2$ dramatically and inhibit the corrosion to stainless steel autoclaves [17].

The influence of the above ligands on the catalytic performance of $CuCl_x$ ($x = 1$ or 2) is not investigated by the Cu coordination compounds as the catalyst, but by the direct mixture of the ligand and $CuCl_x$ as the catalyst. It is very difficult to determine the amount and structure of the Cu coordination compound, which is formed in the oxidative carbonylation of methanol. As a result, it is difficult to understand the essence of the reaction.

Recently it is found that $Cu(phen)Cl_2$ exhibited the higher activity than the equimolar mixture of $CuCl_2$ and Phen in the oxidative carbonylation of methanol [18]. Considering that the corrosiveness of Cl^- to metallic vessels is very high, it is replaced with Br^- [19,20]. In this paper, the copper coordinations with different structures, $Cu(phen)Br_2$, $[Cu(phen)_2Br]Br$ and $[Cu(phen)_3]Br_2$, were prepared through the reaction of 1,10-phenanthroline with cupric bromide in the mixed solution of methanol and ethanol, and their catalytic performances were evaluated. Furthermore, a plausible reaction mechanism was proposed.

2. Experimental

2.1. Materials

All reagents with A.R. purity were purchased from local manufactures and used without further purification. $Cu(phen)Br_2$,

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$[Cu(phen)_2Br]Br$ and $[Cu(phen)_3]Br_2$ were synthesized according to the procedures described by Antunes [21], and were characterized by Fourier-transform infrared spectra.

4 mmol of 1,10-phenanthroline (Phen) in 15.0 ml of ethanol was added dropwise to a solution containing 4 mmol of $CuBr_2$ and 15.0 mL of methanol. Then the mixture was stirred for 30 min at 25 °C. $Cu(phen)Br_2$ was isolated by filtration, washed with methanol (3 × 20 ml) and dried at 45 °C for 24 h in vacuum. The same procedure was conducted for the synthesis of $[Cu(phen)_2Br]Br$ and $Cu(phen)_3Br_2$ using 2 and 3 equivalents of Phen with $CuBr_2$, respectively. $[Cu(phen)_3]Br_2$ was obtained with the evaporation of the solvent at room temperature.

$Cu[(phen)_3]Br_2$: Grass green solid, yield 75.2%. IR (KBr, cm^{-1}): 3054.0, 1622.4, 1581.4, 1513.9, 1422.7, 1340.1, 1142.4, 1098.9, 851.7, 773.5, 721.4, 426.4. $[Cu(phen)_2Br]Br$: Dark green solid, yield 82.4%. IR (KBr, cm^{-1}): 3082.4, 1623.4, 1603.8, 1583.5, 1513.2, 1493.1, 1422.7, 1223.1, 1142.4, 1102.1, 854.8, 781.4, 721.4, 429.5. $Cu(phen)Br_2$: Brick-red solid, yield 85.2%. IR (KBr, cm^{-1}): 3052.0, 1623.4, 1606.9, 1583.1, 1513.8, 1422.8, 1346.2, 1145.5, 1105.1, 851.7, 775.2, 718.3, 430.2.

2.2. Catalyst characterization

Thermogravimetric analysis (TGA) was carried out on a TGA Q50 analyzer under nitrogen at a heating rate of 10 $°C·min^{-1}$ from room temperature to 900 °C.

2.3. Measurement of catalytic activity and selectivity

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

3. Results and Discussion

3.1. Catalytic performances

The activities of Cu complexes were evaluated in the oxidative carbonylation of methanol. As a comparison, the activities of CuBr and $CuBr_2$ and the equimolar mixture of Phen and $CuCl_2$ were also tested. The results are listed in Table 1. When CuBr is used as the catalyst, the turnover number (TON) is 4.4 DMC mol (Cu mol)$^{-1}$ with 95.2% selectivity of DMC. The result might be ascribed to the low solubility of CuBr in methanol, resulting in the decrease of the active centers. $CuBr_2$ could be solved in methanol, but TON is only 5.9 DMC mol·(Cu mol)$^{-1}$ because of its low activity, and dimethoxymethane (DMM) as a by-product is detected with 27.4% selectivity. With the addition of the equimolar amount of Phen, TON and the selectivity of DMC are enhanced to 12.3 DMC mol·(Cu mol)$^{-1}$ and 92.7%, respectively. The result might arise from the formation of the σ–π coordination bond between Phen and Cu(II), which can improve the catalytic activity of $CuBr_2$. However, when the mixture catalyst is replaced with $Cu(phen)Br_2$, TON is increased to 39.9 DMC mol·(Cu mol)$^{-1}$ with 92.5% selectivity of DMC. The results show that: (1) $Cu(phen)Br_2$ is an active species, (2) it is essential for the synthesis of $Cu(phen)Br_2$ from Phen and $CuBr_2$ to maintain enough time, and (3) it is disadvantageous for the in-situ formation of $Cu(phen)Br_2$ at the reaction temperature of 120 °C.

Table 1

Effect of different catalysts on oxidative carbonylation of methanol (reaction conditions: $V_{MeOH} = 50$ ml, $C_{Cu} = 0.011$ $mol·L^{-1}$, $T = 120$ °C, $p = 4$ MPa, $p_{CO}:p_{O_2} = 19:1$, 5 h.)

Catalyst	TON①/DMC mol·(Cu mol)$^{-1}$	S_{DMC}/%	S_{DMM}/%
CuBr	4.4	95.2	4.8
$CuBr_2$	5.9	72.6	27.4
$CuBr_2$ + Phen②	12.3	92.7	7.3
$Cu(phen)Br_2$	39.9	92.5	7.5
$[Cu(phen)_2Br]Br$	4.3	>99.9	0
$[Cu(phen)_3]Br_2$	1.8	>99.9	0
$Cu(phen)Cl_2$[18]	39.0	98.3	1.7
$(C_3H_7)_4NBr/CuBr_2$③[20]	23.5	93.5	

① Turnover number (TON) = n(DMC)/n(copper ion).

② The equimolar mixture of phen and $CuBr_2$ was stirred for 5 min before the reaction started.

③ $p_{CO}:p_{O_2} = 2:1$.

The literatures have reported that the number of ligand affects the activities of the Cu complexes in the oxidation of cyclohexane and toluene [21,22]. The influence of the structures of Cu complexes on the activities was also investigated. As shown in Table 1, TON is only 1.8 DMC mol·(Cu mol)$^{-1}$ over $[Cu(phen)_3]Br_2$, in which copper is hexacoordinated with six Cu–N bonds [23]. The low activity might be ascribed to the following factors: (1) the steric hindrance from three ligands blocks the coordination of Cu(II) with methanol or CO; (2) the saturation of the first coordination sphere inhibits the access of the reacting molecules to the metal center. With the decrease of the ligand number, $[Cu(phen)_2Br]Br$, where copper is pentacoordinated, has the lowly steric hindrance and labile positions occupied by Br^-, so TON is enhanced to 4.3 DMC mol·(Cu mol)$^{-1}$. The mono-Phen complex might be formulated as $Cu(phen)Br_2$ in solution, where copper is tetracoordinated [23]. TON is up to 39.9 DMC mol·(Cu mol)$^{-1}$ due to the lowest steric hindrance and the most labile positions occupied by Br^-. However, its DMC selectivity is lower than that of $[Cu(phen)_2Br]Br$ and $[Cu(phen)_3]Br_2$.

Compared with $Cu(phen)Cl_2$ [18], the activity of $Cu(phen)Br_2$ is slightly high. The literatures have reported that the insertion of CO in monocarbonyl species (Cu(CO)Cl) into the Cu–O bond in the cupric methoxychlide is a key step in the catalytic cycle [24,25], and thus the stability of Cu(CO)Cl is very important. It is well known that CO is an excellent π acceptor, and the Cu–(CO) bond is stabilized by π back-bonding interaction between Cu and CO. Because the electronegativity of Cl (3.0) is higher than that of Br (2.8), the Cu–(CO) bond in Cu(CO)Br is more stable than that in Cu(CO)Cl. Thus, the insertion is easier, resulting in the higher activity for $Cu(phen)Br_2$.

It could be seen from Table 1 that $Cu(phen)Br_2$ exhibits the far higher activity than $(C_3H_7)_4NBr/CuBr_2$, and the reaction conditions are more moderate (the partial pressure of oxygen is below the explosive limit) [20].

3.2. Effect of the thermal stability of the complex on the catalytic activity

The temperature in the oxidative carbonylation of methanol was usually controlled at 110–160 °C, thus the thermal stability of Cu(II) complexes was characterized. As shown in Fig. 1(a), the mass loss of $Cu(phen)Br_2$ is started at 300 °C. This shows that $Cu(phen)Br_2$ is stable in the oxidative carbonylation of methanol. The mass loss is 42.5% from 300 to 470 °C. It is probably caused by the decomposition of Phen because the mass loss is close to 44.7% of Phen in $Cu(phen)Br_2$. The mass loss above 470 °C is attributed to the decomposition of $CuBr_2$.

As listed in Fig. 1(b), the 3.5% mass loss at about 130 °C is due to the removal of crystal water in $[Cu(phen)_2Br]Br$. The mass loss above 270 °C is caused by the decomposition of $[Cu(phen)_2Br]Br$. It is shown that $[Cu(phen)_2Br]Br$ is also stable in the reaction. The mass loss at 100 °C, as shown in Fig. 1(c), arose from the elimination of crystal waters in $[Cu(phen)_3]Br_2$. Its thermal degradation appears above 160 °C. At the same time, it is found that the stability of these catalysts in methanol is similar to that in the nitrogen atmosphere.