Alkoxy carbonylation of EO Catalyzed by the Novel Functionalized Ionic Liquid

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Abstract. A novel carbonyl cobalt polyether functionalized ionic liquid, 1-methyl-3-polyetherimidazole cobalt tetracarbonyl ([CH3(OCH2CH2)8mim][Co(CO)4]), was prepared and characterized by FT-IR. Characteristic absorption peak were found near the 2879cm⁻¹, 1114cm⁻¹ and 1886cm⁻¹, representing the presence of the polyether and [Co(CO)4]⁻ anion structure. The ionic liquid was used as catalyst in alkoxy carbonylation of EO to produce 3-HMP. The effects of temperature, pressure of CO, reaction time and catalyst species on the reaction were studied and the optimal reaction conditions were obtained, that was, 75°C, 7.2Mpa and 12 h. The results showed that [CH3(OCH2CH2)8mim][Co(CO)4] had good activity for alkoxy carbonylation of EO with ethanol and CO. The conversion rate of EO and selectivity of 3-HMP reached to 91.36% and 85.19%, respectively. Not only the ionic liquid could be conveniently separated from the products, but also had good air-stability and reused directly without any treatment for over 10 times, and the conversion rate and selectivity did not go down obviously.

Introduction

In recent years, ionic liquids have been widely used as a new kind of medium and functional materials. Among the researches, the functionalized ionic liquid have attracted considerable attention due to the potential to impart the liquid with specific chemical or physical properties [1-6], and its strong regulatability for numerous chemical work [7,8]. For example, many functionalized organometallic ionic liquids with excellent properties have been synthesized by the transition metal carbonylation fragment into ionic liquids. Compared with the traditional organic metal catalyst, the ionic liquid has relatively low viscosity, better stability and solubility and satisfactory catalytic activity and excellent recycling performance [9, 10], and that is a potential research field as a catalyst for the industry, has a wide application view.

As significant carbonylation catalyst, carbonyl cobalt has been widely used in lots of catalytic reaction. Dyson et al. [11] reported the first case of ionic liquids containing metal carbonyl anionic, and successfully applied in catalyzing the debromination of 2-bromoketones. Church et al. [12] synthesized the complex [(salph)Al(THF)2][Co(CO)4], which is known to carbonylate epoxides, aziridines, and â-lactones, was used to catalyze the synthesis of 1,3-oxazinane-2,4-diones and exhibited good activity. However, since the [Co(CO)4]⁻ was very sensitive to air and poor solubility, the direct application as a catalyst was restricted strongly. So In this communication we report on a new cobalt carbonyl functionalized ionic liquids, 1-methyl-3-polyetherimidazole cobalt tetracarbonyl [CH3(OCH2CH2)8mim] Co(CO)4, which were characterized by FT-IR and successfully used as catalyst in alkoxy carbonylation of EO to produce 3-HMP. The effects of temperature, pressure of CO, reaction time and catalyst species on the reaction were studied and the optimal reaction conditions were obtained, and properties of the catalyst for repeated use were investigated.
The Experiment

Materials and Equipment

Materials. N-methyl imidazole, 98% purity, Beijing Huaye glory Chemical Co., Ltd.; polyethylene glycol 350 (MPEG350), Shenzhen leading Scientific Instruments Co., Ltd., toluene before use with water to give anhydrous MPEG350; Thionyl chloride (SOCl₂), AR, Hefei billion into Experimental Instrument Co., Ltd., vacuum distillation before use; Four potassium cobalt carbonyl (KCo(CO)_4), self-made [13]; high purity nitrogen (99.999%), Weifang Weihe Oxygen Gas Co. Ltd; carbon monoxide (CO), the purity of 99.9%, Jining work together Special Gas Co., Ltd; ethylene oxide (EO), the purity of 99.9%, Jinan New Ze Chemical Co., Ltd.; methanol, AR , Nanjing Chemical Reagent Co., Ltd., Prior to use CaH micro-boiling, reflux 2h, evaporated under reduced pressure to obtain anhydrous methanol; the other reagents in the experiment were of analytical grade or chemically pure, commercially available.

Equipment. Gas chromatograph GC-7806, Beijing Shi Yan for the special analysis Instrument Co., Ltd; Gas chromatography - mass spectrometry 7890A-GC/5975C-MSD, Agilent Co; Fourier infrared spectrometer TENSOR 27, Germany Bruker Corporation; Collector thermostat heating magnetic agitator DF-101S , Shanghai instrument Co., Ltd.

Reaction Principle. As shown in figure 1, the synthetic route used to prepare the 1-methyl-3-polyetherimidazole cobalt tetracarbonyl described herein is illustrated as follows:

![](attachment:image.png)

Figure 1. The synthetic route of the 1-methyl-3-polyetherimidazole cobalt tetracarbonyl.

The Preparation of Functionalized Ionic Liquids. Weigh MPEG 3506.98 g (19.95 mmol), toluene 130ml within 250mL three-neck flask and a reflux condenser mounting means and the constant pressure dropping funnel, 8.55 g (22.5 mmol, excess) SOCl₂ was dissolved in 20 ml of toluene with slowly adding dropwise at room temperature. Weigh 2.25g (27.15 tendency, excess) N-methylimidazole, 75mL of toluene and the above 250ml product three necks flask, condenser for 24 h, 90℃, after completion of the reaction, toluene was removed by distillation under reduced pressure and excess methyl-N-imidazole, was a red-brown liquid ionic polyether-methyl-3-chloro-imidazole.

Under the protection of N2, the THF solution of tetracarbonyl cobalt potassium 60ml (including [CO (CO) -- 19.95mmol) into a 250ml three flask, with a constant pressure drop funnel dripping slowly a THF solution of [CH₃ (OCH₂CH₂) 8bm|Cl, room temperature water bath stirring 2h, centrifuged to remove KCl precipitation, evaporation under reduced pressure to THF to ink green.
viscous liquid, at low temperature, avoiding light, storage under N₂ protection. According to the molecular weight of MPEG calculated polyether chain length is about 8.

**The Hydrogen Ester Reaction of Ethylene Oxide.** Methanol 15 ml, [CH₃(OCH₂CH₂)₈mim][Co(CO)₄] in THF 30 ml were added into 75 ml stainless steel reaction kettle, replaced three times with CO, close the valve, cryogenic storage 0.5h. And then injected cryopreserved 0.08mol EO by feeding the pipeline at low temperature. Through a pressure regulating valve to achieve a reaction pressure of CO. Gas chromatography - mass spectrometry and gas chromatography analysis of the reaction product selectivity structure and distribution, calculate EO conversion and 3-hydroxy-propionic acid methyl ester (3-HMP). In the circulation of catalyst recycling experiment, the ionic liquid catalyst after the reaction was added to separate the solvent and reactant for the next reaction directly. The synthetic route used to prepare the 1-methyl-3-polyetherimidazole cobalt tetracarbonyl described herein could be written as:

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{Ionic liquid catalyst}} \text{HOCH}_2\text{CH}_2\text{COCH}_3
\]

(1)

**The Results and Discussion**

**Characterization of Functionalized Ionic Liquids**

MPEG and chlorinated MPEG infrared spectra, shown in Figure1, 3412.56 cm⁻¹ (-OH stretching vibration), 2871.01 cm⁻¹ (-CH₂ - stretching vibration), 1110.78 cm⁻¹ (C-O-C stretching vibration).

As shown in Figure 2(a), after the MPEG reaction with thionyl chloride, the terminal hydroxyl absorption peak was significantly reduced, indicating MPEG terminal hydroxyl groups have been substituted with Cl.

As shown in Figure 2(b), the IR spectrum of the ionic liquid in addition to the polyether chain characteristic absorption peaks (2879.26 cm⁻¹: -CH₂- stretching vibration; 1114.04 cm⁻¹: C-O-C stretching vibration), an imidazole ring C-H stretching vibration occurs at 3109.71 cm⁻¹, 1644.69 cm⁻¹ is an imidazole ring C = C stretching vibration, and 1574.44 cm⁻¹ is an imidazole ring C = N stretching vibration, within 1281.34 cm⁻¹, 1248.02 cm⁻¹ for the imidazole ring plane CH bending vibration characteristic peaks above indicates a presence of the imidazole ring structure; 1886.07 cm⁻¹ for a typical end carbonyl absorption peaks, belongs to [Co(CO)₄]⁻ ion [14-15].

Figure 2. MPEG and chloro-MPEG IR spectra(a) and [CH₃(OCH₂CH₂)₈mim][Co(CO)₄] IR spectra(b).

As shown in Figure 2(b), the IR spectrum of the ionic liquid in addition to the polyether chain characteristic absorption peaks (2879.26 cm⁻¹: -CH₂- stretching vibration; 1114.04 cm⁻¹: C-O-C stretching vibration), an imidazole ring C-H stretching vibration occurs at 3109.71 cm⁻¹, 1644.69 cm⁻¹ is an imidazole ring C = C stretching vibration, and 1574.44 cm⁻¹ is an imidazole ring C = N stretching vibration, within 1281.34 cm⁻¹, 1248.02 cm⁻¹ for the imidazole ring plane CH bending vibration characteristic peaks above indicates a presence of the imidazole ring structure; 1886.07 cm⁻¹ for a typical end carbonyl absorption peaks, belongs to [Co(CO)₄]⁻ ion [14-15].
Ionic Liquid Catalytic EO Hydroesterification Reaction

**Effect of Temperature on the Reaction.** Figure 3(a) investigated the functional ionic liquid catalyst for the catalytic activity of EO hydroesterification reaction, at different temperatures. In this reaction, the pressure is 7.2Mpa, and the time of reaction is 12 h, then the result of EO hydroesterification is concluded under different temperature. As shown in Figure 3(a), effect of temperature is larger, and the reaction conversion and reaction selectivity is lower, and maybe due to the activity of catalyst is low under low temperature. With the increase of temperature, the conversion rate of EO and the selectivity of 3-HPM were Rise, and the selectivity of EO was lower, after 75 °C selectivity decreases, this may be because the temperature is not only beneficial to EO ring-opening esterification, and can promote the catalyst for the activation of substrates, overcome the reaction energy barrier, to ensure the rapid reaction. The temperature is too high and may cause a series of adverse reactions, so the reaction temperature is 75.

![Figure 3(a)](image)

**Effect of CO Pressure on the Reaction.** Figure 3(b) examines the reaction temperature is 75 °C, the reaction time of 12 h, under different pressure, the functional ionic liquid catalysts for the catalytic activity of EO hydroesterification reaction. The Figure 3(b) shows that pressure of CO have bigger influence on the reaction, CO reaction, under low pressure, the conversion of EO and selectivity of 3-HMP are low, which is because the reaction is gas-liquid two-phase reaction, and low reaction pressure is not conducive to the reaction.with the increase of pressure, catalytic activity of ionic liquid catalyst improves, and because the CO pressure rises, that is beneficial to the addition reaction between CO and Co-Alkyl, and cobalt carbonyl can effectively promote the catalytic effect, thus

![Figure 3(b)](image)
promote the hydroesterification reaction. However, when the reaction pressure exceeds 7.2 Mpa, the conversion rate of EO changes slowly, and the selectivity of 3-HMP is decreased due to the Side effect, so the most suitable reaction pressure is 7.2 Mpa.

**Effect of Reaction Time on Reaction.** Figure 3(c) examines the reaction temperature is 75 °C, CO pressure 7.2 Mpa, in different reaction time, functionalized ionic liquid catalyst for the catalytic activity of EO hydroesterification reaction. The Figure 3(c) shows that compared with the reaction pressure and reaction temperature, reaction time for EO hydroesterification reaction less affected. with the increase of time, the conversion of EO, increase amplitude is small, after 12 h and 3 - HMP selectivity decreased obviously. Although this is because the time is beneficial to reaction, but the long reaction time will greatly enhance the probability of adverse events and can make the product break down, or even led to the decrease of the selective polymerization. So the optimum reaction time is 12 h.

**Effect of Different Catalysts on the Reaction Performance.** In this experiment, the catalytic performance of different catalysts for EO hydrogenation was investigated. The reaction temperature was 75, the pressure was 7.2 Mpa, the time was 12 h, and the catalytic effect of different catalysts was shown in Table 1

<table>
<thead>
<tr>
<th>Number</th>
<th>Catalyst type</th>
<th>Conversion rate (%)</th>
<th>3-HMP selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CoCl₂</td>
<td>56.40</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Co₂(CO)₈</td>
<td>90.76</td>
<td>70.45</td>
</tr>
<tr>
<td>3</td>
<td>KCo(CO)₄</td>
<td>93.12</td>
<td>79.38</td>
</tr>
<tr>
<td>4</td>
<td>[CH₃(OCH₂CH₂)₃mim][Co(CO)₄]</td>
<td>91.36</td>
<td>85.19</td>
</tr>
</tbody>
</table>

Table 1 shows that EO conversion was 56.40%, used CoCl₂ as the catalyst, but the selectivity of 3-HMP is almost zero, when the Co₂(CO)₈ and KCo(CO)₄ as catalyst, EO conversion rate were higher, 90.76% and 93.12% respectively, and selectivity was 70.45% and 79.38%, while we prepared as a catalyst in ionic liquids, the conversion rate reached 91.36 percent, and the selectivity was as high as 85.19%. This is probably because the active ingredient cobalt carbonyl catalysts are HCo (CO)₄ [15], then Co₂(CO)₈ is further reacted with an active hydrogen action into real catalytic precursor HCo (CO)₄ under certain conditions, so that the activity of it is relatively low, and the catalyst we synthesized can be directly catalysis as catalytic precursor.

**Table 2. Recycling efficiency of the ionic liquids in the alkoxy carbonylation of EO.**

<table>
<thead>
<tr>
<th>Number</th>
<th>Cycles</th>
<th>Conversion rate (%)</th>
<th>selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>91.36</td>
<td>85.19</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>89.40</td>
<td>86.03</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>90.72</td>
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</tr>
<tr>
<td>4</td>
<td>3</td>
<td>90.10</td>
<td>83.31</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>88.34</td>
<td>82.71</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>88.71</td>
<td>84.27</td>
</tr>
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</tr>
<tr>
<td>10</td>
<td>9</td>
<td>72.34</td>
<td>82.54</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>70.71</td>
<td>83.92</td>
</tr>
</tbody>
</table>

**Catalyst Recycling Performance.** Under the optimum conditions obtained above reaction, after the reaction with n-heptane and the product extracted with separated ionic liquid, and then directly adding a solvent and reactant for the next reaction without any treatment, we investigated the recycled ionic liquid performance. Table 2 shows that the ionic liquid catalyst is reused up to 10 times, although the conversion rate has dropped, but the appropriate reaction time, EO conversion was still
able to reach 90%, and the selectivity of 3-HMP has been around 84%. However, with \( \text{Co}_2(\text{CO})_8 \) and \( \text{KCo} (\text{CO})_4 \) as the catalyst, since the air is extremely sensitive, almost circulation can not be achieved. The functional ionic liquid catalyst prepared in this experiment both with a stable ionic bonds have long polyether chain wrapped, so the stability of the air has greatly improved, which can be recycled many times.

**Conclusion**

1. In this work, cobalt carbonyl functional polyether ionic liquid hydrogen having a group of catalytically active ester was successfully prepared, and the structure were characterized using infrared spectroscopy, which found 2879.26 cm\(^{-1}\), 1114.04 cm\(^{-1}\) and 1886.07 cm\(^{-1}\) are the strong characteristic absorption peak, proving that the polyether structure \([\text{Co} (\text{CO})_4]^-\) presence.

2. The ionic liquid was used as catalyst in alkoxy carbonylation of EO to produce 3-HMP. The effects of temperature, pressure of CO, reaction time and catalyst species on the reaction were studied and the optimal reaction conditions were obtained, that was, 75°C, 7.2Mpa and 12 h. The results showed that \([\text{CH}_3(\text{OCH}_2\text{CH}_2)_8\text{mim}] [\text{Co(CO)}_4]\) had good activity for alkoxy carbonylation of EO with ethanol and CO. The conversion rate of EO and selectivity of 3-HMP reached to 91.36% and 85.19%, respectively under the optimum reaction conditions.

3. The recycling performance was examined, concluding that the functional ionic liquid catalyst has a stable ionic bond and a longer polyether chain, relatively stable in the air, which can be reused up to 10 times, and the conversion rate and selectivity did not go down obviously.

**References**


