

# Synthesis and evaluation of stable, efficient, and recyclable carbonylation catalysts: Polyether-substituted Imidazolium carbonyl cobalt ionic liquids



Zhiguo Lv\*, Yongfei Jiang, Chao Zhou, Zhenmei Guo\*, Xiuling Ma, Qiang Chen, Tao Nie, Hongbing Song

College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China

## ARTICLE INFO

### Article history:

Received 31 October 2015  
Received in revised form 13 January 2016  
Accepted 14 January 2016  
Available online 19 January 2016

### Keywords:

Bifunctionalized ionic liquids  
Carbonylation catalyst  
Thermoregulated biphasic system  
Imidazolium  
Carbonyl cobalt

## ABSTRACT

The synthesis and catalytic performance of stable, efficient, and recyclable multi-functionalized ionic liquid catalysts are reported for the first time. Through an optimized synthetic strategy, a series of polyether-substituted imidazolium cobalt tetracarbonyl salts,  $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$  ( $n = 8, 15,$  and  $22$ , bim = butylimidazolium), and their intermediates, were successfully synthesized and characterized by IR, UV–vis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and TGA. The stability, solubility, and critical solution temperature of the ionic liquids were also determined. A thermoregulated phase-separation catalysis system for the hydroesterification of olefins has been established based on the above multi-functionalized ionic liquid catalyst. The results show that this catalysis system has a high recycling efficiency, and provides a potential method for an environmentally benign carbonylation process.

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## 1. Introduction

In recent years, functionalized ionic liquids (FILs) have been paid increasing research attention because of their ability to be tailored for various chemical tasks [1,2]. Many transition metal carbonyl species have been introduced into FILs, producing organometallic ionic liquids [3–5], which, while having comparable catalytic activity to conventional organometallic catalysts, show some improvements, such as lower viscosity, better stability, improved solubility, and excellent recovery [6,7].

PEG-based ionic liquids are a new appealing group of solvents making the link between two distinct but very similar fluids: ionic liquids and poly(ethylene glycol)s. They find applications across a range of innumerable disciplines in science, technology, and engineering. In the last two years, the possibility to use these as alternative solvents for organic synthesis and catalysis has been increasingly explored [8].

The cobalt tetracarbonyl anion,  $[\text{Co}(\text{CO})_4]^-$ , is one of the most important active catalytic species and has been widely used in a number of catalytic reactions [9–16,22]. Although some ionic liquid compounds containing  $[\text{Co}(\text{CO})_4]^-$  have been successfully synthesized and employed in some reactions, most of them are homogeneous catalysts, which are difficult to recycle. In addition, because it is unstable and sensitive to air, the direct use of  $[\text{Co}(\text{CO})_4]^-$  is limited [5].

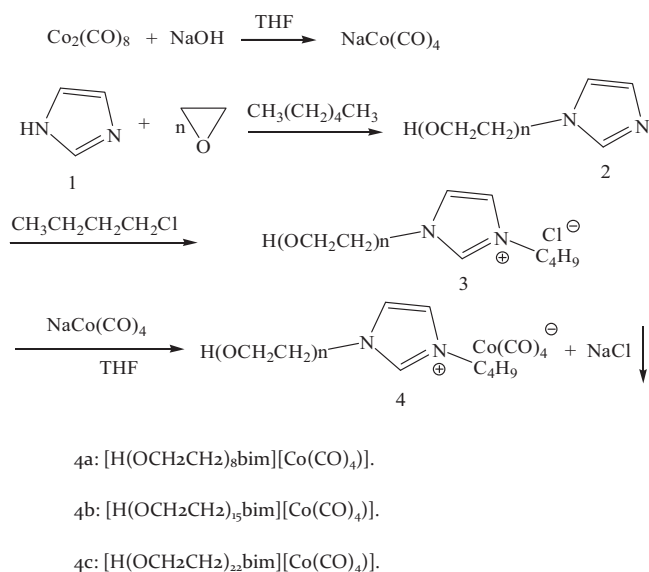
The search for a way to combine the advantages of homogeneous catalysis, such as ease of modulation, and heterogeneous catalysis, such as ease of recycling, is one of the most exciting challenges in modern chemistry. Indeed, various efficient immobilization methods for homogeneous catalyst have been developed in recent years through the use of methods such as liquid–liquid organometallic biphasic catalysis and heterogenization of molecular catalysts on solid supports. However, the advantages of these methods come at the expense of catalytic activity [17].

For the purpose of the recycling of catalysts, functionalized ionic liquid methodology was tentatively applied to the ionic liquid/organic biphasic catalysis system [18]. For example, we have shown that  $[\text{bmim}][\text{Co}(\text{CO})_4]$  (bmim = 1-butyl-3-methylimidazolium) is an efficient catalyst for the hydroesterification of ethylene oxide [14]. It was reported that introducing the polyether chain to the ligands or ionic liquids not only facilitates dispersion in the reaction system by reducing ionic

Abbreviations: CST, critical solution temperature; TPSC, thermoregulated phase-separation catalysis; FIL, functionalized ionic liquid; bim, butylimidazolium; bmim, 1-butyl-3-methylimidazolium.

\* Corresponding authors.

E-mail addresses: [lvzhiguo@qust.edu.cn](mailto:lvzhiguo@qust.edu.cn) (Z. Lv), [gzhennm@sina.com](mailto:gzhennm@sina.com) (Z. Guo).



**Scheme 1.** Synthesis of polyether-substituted imidazolium carbonyl cobalt ionic liquids.

liquid viscosity, but also allows catalysts to be thermoregulated [19].

In this paper, we report the convenient synthesis of a series of polyether-substituted imidazolium cobalt carbonyl ionic liquids, as well as their detailed characterization and catalytic performance in hydroesterification. Moreover, preliminary studies on the application of these functionalized ionic liquids in a thermoregulated phase-separation catalysis system (TPSC) have been performed by applying this system to the hydroesterification of 4-isobutyl styrene.

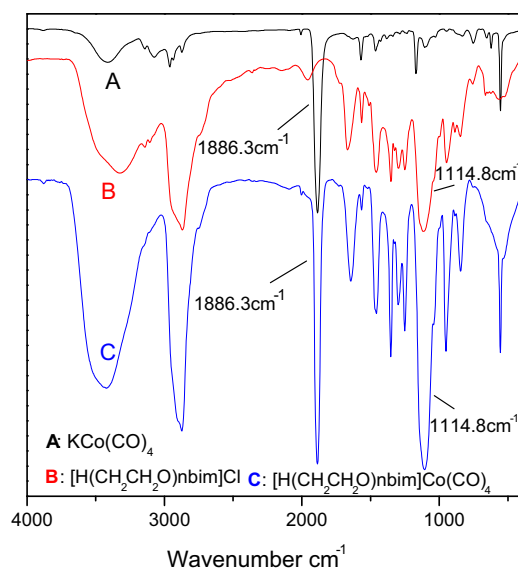
## 2. Results and discussion

### 2.1. Synthesis of the polyether-substituted imidazolium carbonyl cobalt ionic liquids

The synthesis of  $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$  **4** is shown in Scheme 1.  $\text{NaCo}(\text{CO})_4$  was prepared by a method previously reported in the literature [20]. Firstly, ethylene oxide was reacted with imidazole to obtain 3-poly(ethylene glycol) imidazole **2** containing different numbers of polymerized ethylene oxide units ( $n=8, 15,$  and  $22$ ). Then, **2** was reacted with  $n$ -butyl chloride to produce chloro-substituted 1-butyl-3-poly(ethylene glycol) imidazole **3**, i.e.,  $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}]\text{Cl}$ , **3**. Finally, compounds **4** were obtained by the ion exchange reaction of **3** with  $\text{NaCo}(\text{CO})_4$ . The resultant compounds **4** were red–brown, viscous liquids at room temperature.

### 2.2. Solubility

The solubilities of **4** ( $n=8, 15,$  and  $22$ ) were determined qualitatively in several common solvents. All three salts show similar solubility. They are all well dissolved in polar organic solvents, such as methanol, ethanol, acetone, and water, and are insoluble in some weakly polar solvents such as ether, cyclohexane, and  $n$ -hexane, most likely due to existence of the ionic bond. Moreover, the length of the polyether chain also has a significant effect on the solubility. In some solvents, such as ethyl acetate, toluene, THF and 1,4-dioxane, the solubility of **4** increases with an increase in the length of the polyether chain. According to the literature  $[\text{bmim}][\text{Co}(\text{CO})_4]$  is almost insoluble in water [21]. However, all the versions of **4** are highly soluble in water because of the polyether



**Fig. 1.** IR Spectra of  $\text{KCo}(\text{CO})_4$ ,  $[\text{H}(\text{OCH}_2\text{CH}_2)_{22}\text{bim}]\text{Cl}$  and  $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$ .

chain, which can form hydrogen bonds with water through the alternate ether linkages and the hydroxyl terminus. This solubility in water removes the need for organic solvents, making our catalyst potentially applicable to green chemistry.

### 2.3. Stability

These compounds have shown comparatively better air stability than analogous conventional  $[\text{Co}(\text{CO})_4]^-$  salts, such as  $\text{NaCo}(\text{CO})_4$  and  $\text{KCo}(\text{CO})_4$ , which are easily oxidized by air because of the  $-1$  valence of Co, due to the strong effect of the electron pair (it can be seen by IR spectrum in Fig. 1). In addition, their air stability significantly increases with the value of  $n$ . No obviously changes in the physical appearance and IR spectrum of  $[\text{H}(\text{OCH}_2\text{CH}_2)_{22}\text{bim}][\text{Co}(\text{CO})_4]$  are observed after exposure to air for 32 h at room temperature.

### 2.4. Infrared studies

In all infrared spectra of  $\text{Na}[\text{Co}(\text{CO})_4]$ ,  $\text{K}[\text{Co}(\text{CO})_4]$ , and compounds **4a–c**, the characteristic carbonyl  $T_2$  absorption bands near  $1886\text{ cm}^{-1}$  are found, indicating the presence of  $[\text{Co}(\text{CO})_4]^-$ . However, these absorption bands are slightly different for the different compounds. Generally, compared with the corresponding pyridinium compounds, the carbonyl absorption band for the imidazolium compounds is shifted to higher wave numbers [5], and with the change of polyether chain length, the carbonyl stretching band appears to be red-shifted, which usually indicates the presence of interionic hydrogen bonds between the ion pairs. In the IR spectra of compounds **4a–c**, the appearance of the symmetry-forbidden  $A_1$  bands near  $2003\text{ cm}^{-1}$  indicate that  $[\text{Co}(\text{CO})_4]^-$  has a certain degree of torsion deformation compared with the usual tetrahedral structure. This may be caused by the hydrogen bonding between the tetracarbonyl cobalt and the cation. In contrast, the single band at  $1883\text{ cm}^{-1}$  for crystalline  $[\text{PPN}][\text{Co}(\text{CO})_4]$  ( $\text{PPN}=(\text{Ph}_3\text{P})_2\text{N}^+$ ) is assigned to the  $T_2$  mode of undistorted tetrahedral  $[\text{Co}(\text{CO})_4]^-$  [20]. The IR spectrum of  $\text{NaCo}(\text{CO})_4$  shows a split carbonyl peak at  $2014\text{ cm}^{-1}$ , while the  $T_2$  bands of **4a–c** are split in another way (Table 1), which is similar to previous observations of  $\text{Q}^+[\text{Co}(\text{CO})_4]^-$  ( $\text{Q}=N$ -methyl-1-quinolinium) [23]. It has been demonstrated by Bockman and Kochi that the splitting of carbonyl peaks provides a means for the effective and accurate

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