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Catalytic performance of [Bmim][Co(CO)$_4$] functional ionic liquids for preparation of 1,3-propanediol by coupling of hydroesterification-hydrogenation from ethylene oxide

Zhenmei Guo, Hengsheng Wang, Zhiguo Lv*, Zhihui Wang, Tao Nie, Weiwei Zhang

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

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ABSTRACT

In this paper, synthesis of 1,3-propanediol (1,3-PDO) through coupling of hydroesterification-hydrogenation from ethylene oxide (EO) catalyzed by 1-butyl-3-methylimidazolium cobalt tetracarbonyl [Bmim][Co(CO)$_4$] functional ionic liquid which was prepared by metathesis reaction between [Bmim]Cl and KCo(CO)$_4$ has been studied. The structure of [Bmim][Co(CO)$_4$] was characterized by FT-IR and ^{1}H NMR. Using [Bmim][Co(CO)$_4$] as catalyst and [Bmim]PF$_6$ as solvent, 1,3-PDO was prepared for the first time by coupling of hydroesterifaction of EO and hydrogenation of methyl 3-hydroxypropionate (3-HPM). The yield of 3-HPM can reach 90.8%, while the yield of 1,3-PDO up to 82.9%. The catalyst can be separated from the product mixture by extraction with deionized water and recycled several times without significant loss of catalytic efficiency. A possible reaction mechanism has also been proposed.

1. Introduction

1,3-Propanediol (1,3-PDO) as a bifunctional organic compound could potentially be used for many synthesis reactions, in particular as a monomer for polycondensing to produce polyesters, polyethers and polyurethanes. Polyesters based on 1,3-PDO have unique features that are difficult to obtain from other glycols. For instance, poly(trimethylene terephthalate) (PTT), a new polyester based on 1,3-PDO, has the elastic recovery of nylon and the chemical resistance of polyester [1]. Various manufacturing processes for 1,3-PDO have been developed including routes based on acrolein, ethylene oxide (EO) and glucose or glycerol [2]. The low conversion efficiency of the acrolein process, as well as the hazardous nature of acrolein, has spurred a great deal of interest in producing 1,3-PDO from other chemical sources. In recent years, the EO-based route has been most intensively studied, through carbonylation of EO followed by hydrogenation of the intermediate 3-hydroxypropionaldehyde (3-HPA) or methyl 3-hydroxypropionate (3-HPM) [3,4]. However, the intermediate 3-HPA was unstable and could formlow polymerandethylidene ether easily [5]. Although efforts have been made so far and some progress has also been achieved, the processes for preparing 1,3-PDO by hydrogenation of 3-HPM in the presence of copper-based catalysts have low reaction rates and low product yields, because activities and stability of the catalyst and selectivity to 1,3-PDO were unfavorable. Meanwhile, the mono-catalytic systems for hydroesterification of EO to 3-HPM intermediate were less active or stable and were also difficult to recover and recycle [6–8].

Ionic liquids (IL), in particular, consisting of 1-R-3-methylimidazolium (Rmim) cations and their counter anions, have attracted more and more attention due to their unique chemical and physical properties of nonvolatile, nonflammability, thermal stability, and controlled miscibility [9–17]. Over the last few years, ionic liquids have successfully been applied as alternative solvents for homogeneous catalysis [18]. Recently, the functional ionic liquid catalysts have become more important in homogeneous catalysis as catalysts, because functional ionic liquid catalysts could be superior to traditional catalysts in the catalytic activity, stability and selectivity for many reactions, but the catalysts cannot be recycled in most cases [9,18–21].

In this paper, we report on the application of [Bmim][Co(CO)$_4$] functionalized ILs as catalyst for coupling reactions of hydroesterifaction of EO and hydrogenation of methyl 3-hydroxypropionate to prepare 1,3-propanediol. Functional ionic liquid [Bmim][Co(CO)$_4$] as a catalytic active organometallic ionic liquid was first prepared by P.J. Dyson in 2001 [22], but the catalytic performance of the above mentioned new organometallic

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* Corresponding author. Tel./fax: +86 532 84022719.
E-mail address: lvzhiguo@qust.edu.cn (Z. Lv).

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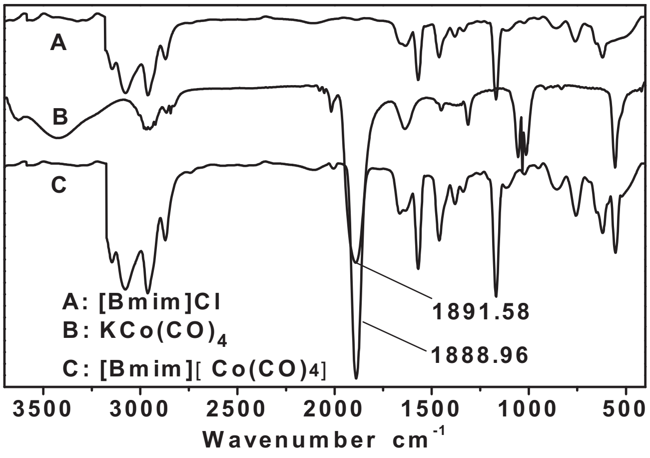


Fig. 1. IR spectrums of $KCo(CO)_4$, [Bmim]Cl and [Bmim][$Co(CO)_4$].

compound was less studied. As far as we are aware, use of this class of ILs as a catalyst for coupling reactions of hydroesterifaction and hydrogenation has not been previously reported. Using [Bmim][$Co(CO)_4$] as catalyst and [Bmim]PF_6 as solvent, 3-HPM was prepared by hydroesterification of EO and 1,3-PDO was prepared by hydrogenation of 3-HPM. The catalytic system can be separated from the product mixture by extraction with deionized water and recycled three times without significant loss of catalytic efficiency. A possible reaction mechanism has been proposed , and the optimum reaction conditions were also obtained by single-factor experiments.

2. Experimental section

2.1. General remarks

1-Chlorobutane, 1-methylimidazole and methanol were simply distilled under nitrogen atmosphere before being used. Potassium borohydride and cobalt chloride were obtained from Sinopharm Chemical Reagent and were used as received without further purification. Hydrogen (99.9%) and carbon monoxide (99.9%) were supplied by Heli Gases and were used as received.

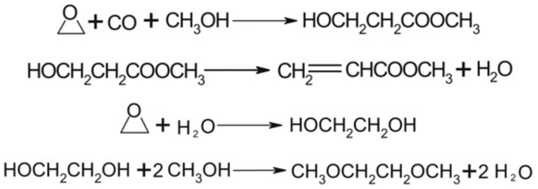
Physical data of 3-HPM: molecular weight 104.10, relative density(25 °C, $H_2O = 1$)1.09, boiling point 145 °C. 1,3-PDO: molecular weight 76.1, relative density(25 °C, $H_2O = 1$)1.05, boiling point 211 °C.

2.2. Catalyst preparation

$KCo(CO)_4$ was prepared in a 100-mL stainless steel autoclave. After calculated amounts of potassium borohydride and cobalt chloride were charged into the reactor, the autoclave was purged with CO three times and pressurized to the desired level. A specified temperature (1–5 °C) was maintained in an ice-bath. After 4 h, KCl and unreacted materials were removed by filtration , affording a methanol solution of $KCo(CO)_4$.

[Bmim]Cl was synthesized by reaction of 1-methylimidazole and 1-chlorobutane [n(1-methylimidazole):n(1-chlorobutane) = 1:1.1]. In a typical experiment, 1-chlorobutane and 1-methylimidazole were added to a flask and then refluxed for 48 h. Unreacted materials were removed by washing with ethyl acetate, and then ethyl acetate was removed by distillation under reduced pressure.

The reaction of K[$Co(CO)_4$] and [Bmim]Cl was carried out in a 100-mL stainless steel autoclave. Typically, [Bmim]Cl and methanol solution of $KCo(CO)_4$ were charged into the reactor. The autoclave was purged with CO three times and the contents were heated to 25 °C and maintained 24 h, then precipitate (KCl) was removed by filtration, and methanol was removed by distillation under reduced pressure affording an intense blue-green colored liquid [Bmim][$Co(CO)_4$]. The characterization of [Bmim][$Co(CO)_4$] was made on Brucker VERTEX 70 Fourier Transform Infrared Spectrometer (Liquid Membrane Method) and BrukerDRX-500 Nuclear Magnetic Resonance Spectrometer (500 MHz, D_2O).



Scheme 1. The reaction equations of the hydroesterification of EO.

2.3. Hydroesterification/hydrogenation reaction

Hydroesterification reaction of EO was conducted in a 100-mL stainless steel autoclave equipped with a magnetic drive stirrer and an electrical heater. For the catalytic experiments, 1.02 mmol of Catalyst, 2.04 mmol of promoter, 102 mmol (4.49 g) of EO and 40.8 mmol of solvent were placed in the autoclave. The reactor was pressurized with CO, and then heated to a specified temperature.

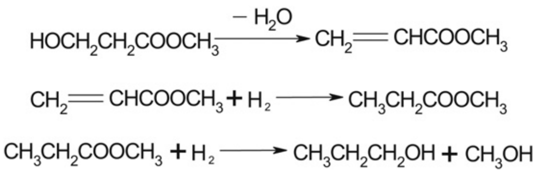
Hydrogenation reaction of 3-HPM was conducted in a 60-mL stainless steel autoclave. In a typical experiment, 1.02 mmol of Catalyst, 2.04 mmol of promoter, 20.4 mmol (2.12 g) of 3-HPM and 40.8 mmol of solvent were placed in the reactor. After H_2 was then charged, the reactor was pressurized to the desired pressure and was then heated to a specified temperature.

After completion of the reaction, autoclave was cooled with ice-water and slowly depressurized to atmospheric pressure through a cold trap, the product mixture was analyzed by means of GC and GC–MS. The catalyst was then separated from the product mixture by extraction with deionized water, and then it was dried for next run. Co leaching was analyzed by means of inductively coupled-plasmaopticalemission spectroscopy(ICP). Gas chromatographic analysis was made on a Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector and HP-5 capillary column (0.32 μm × 50 m). The identity of reaction products was confirmed with a Hewlett Packard 6890-5973 MSD GC–Mass spectrometer.

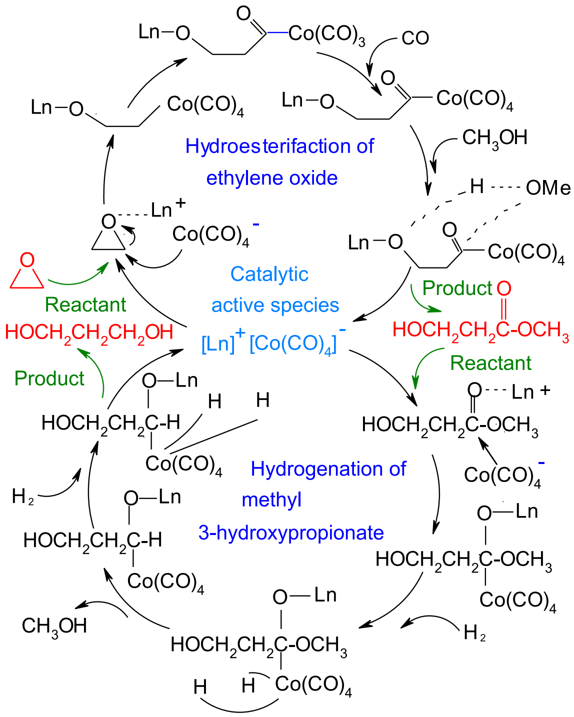
3. Results and discussion

3.1. Catalyst characterization

Spectroscopic data of [Bmim][$Co(CO)_4$]: ^1H NMR: δ8.68 (s, 1H), 7.44 (m, 1H), 7.42 (m,1H), 4.18 (t, 2H), 3.73 (s, 3H), 1.85 (m, 2H), 1.32 (m, 2H), 0.92 (m, 2H). IR: v 3076.12 (ν_{C-H}, aromatic), 2961.60 and



Scheme 2. The reaction equations of the hydrogenation of 3-HPM.



Scheme 3. Proposed mechanism of hydroesterification/hydrogenation.

2870.79 (ν_{C-H}, aliphatic), 1888.96 ($\nu_{C=O}$), 1664.40 ($\nu_{C=C}$, aromatic), 1569.90, 1461.43 and 1380.22 (δ_{C-H}), 1169.14 (δ_{C-H}, aromatic), 758.08, 621.03, 554.72.

IR spectrum of $KCo(CO)_4$, [Bmim]Cl and $[Bmim][Co(CO)_4]$ is shown in Fig. 1. Obviously, there is no peak in IR spectrum (A) of [Bmim]Cl from 2000 cm^{-1} to 1700 cm^{-1}. IR spectrum (B) reveals a strong band at 1891.58 cm^{-1} for the $[Co(CO)_4]^-$ anion in $KCo(CO)_4$. IR spectrum (C) shows the strong absorption of carbonyl group at 1888.96 cm^{-1}, and illuminates the existence of $[Co(CO)_4]^-$ anion in $[Bmim][Co(CO)_4]$.

3.2. Analysis of the reaction products

According to the GC and GC–MS analysis, we found that the by-products of hydroesterification were $CH_2{=}CHCOOCH_3$, $HOCH_2CH_2OH$, $CH_3OCH_2CH_2OCH_3$ and the by-products of hydrogenation were $CH_2{=}CHCOOCH_3$, $CH_3CH_2COOCH_3$, $CH_3CH_2CH_2OH$, CH_3OH. The reaction equations were shown as Scheme 1 and Scheme 2.

3.3. Reaction mechanism

It is well established that the active species for $[Bmim][Co(CO)_4]$ catalyzed hydroesterification of EO and hydrogenation of 3-HPM was an ionic species, $[L_n]^+[Co(CO)_4]^-$ [23–25], when a Lewis base (L) was used as a promoter (e.g. Imidazole , etc.) . The Lewis acidic cationic species $[L_n]^+$ was thought to be responsible for the coordination and activation of EO or 3-HPM, while anionic species $[Co(CO)_4]^-$ was accountable for nucleophilic attack on the less hindered carbon atom of the coordinated EO or 3-HPM and CO or H_2 insertion, the proposed mechanism is shown in Scheme 3.

3.4. The catalytic performance of different catalysts

The catalytic performance of different catalysts for hydroesterification of EO and hydrogenation of 3-HPM were studied (Table 1, entries 1–5). Obviously, the catalytic activity of $[Bmim][Co(CO)_4]$ was best among the above-mentioned catalysts. It seemed that the introduction of imidazolium ionic liquid not only increased the stability of catalyst in operation system, but also avoided catalyst leaching when it was separated from the product mixture.

3.5. Effect of the solvents on hydroesterification/hydrogenation

Comparing the results of hydroesterification of EO and hydrogenation of 3-HPM catalyzed by $[Bmim][Co(CO)_4]$ in different solvents, the effect of the solvents on the catalytic performances was obvious (Table 1, entries 6–10), the catalytic activity was better when imidazolium ionic liquid was used as a solvent and $[Bmim]PF_6$ was the most appropriate solvent for hydroesterification and hydrogenation. Therefore $[Bmim]PF_6$ was used as a solvent in further experiments.

3.6. Effect of the promoters on hydroesterification/hydrogenation

We tested the promoting effect of the promoter on hydroesterification and hydrogenation catalyzed by $[Bmim][Co(CO)_4]$. Obviously, imidazole was highly effective for the ring-opening of

Table 1
Effect of solvents, catalyst and promoter on hydroesterification/hydrogenation.

Entry	Catalyst	Solvent	Promoter	Hydroesterification[a]		Hydrogenation[b]	
				EO conversion (%)	Selectivity to 3-HPM (%)	3-HPM conversion (%)	Selectivity to 1,3-PDO (%)
1	None	$[Bmim]PF_6$	Imidazole	0	0	0	0
2	$CoCl_2$			0	0	0	0
3	$Co_2(CO)_8$			78.2	62.7	73.6	70.1
4	$KCo(CO)_4$			85.3	78.2	82.9	75.8
5	$[Bmim][Co(CO)_4]$			98.1	92.6	99.2	83.6
6	$[Bmim][Co(CO)_4]$	None	Imidazole	73.6	30.8	72.5	16.2
7		methanol		89.2	68.5	84.3	60.9
8		Tetrahydrofuran		91.6	72.4	92.9	64.8
9		$[Bmim]BF_4$		97.9	86.5	98.7	81.4
10		$[Bmim]PF_6$		98.1	92.6	99.2	83.6
11	$[Bmim][Co(CO)_4]$	$[Bmim]PF_6$	None	26.8	16.1	26.8	16.1
12			Pyridine	52.3	38.6	52.3	38.6
13			Imidazole	98.1	92.6	99.2	83.6
14			Triphenyl phosphine	87.8	80.6	87.8	78.6
15			Tributyl phosphine	88.9	82.7	88.9	76.3

[a] Hydroesterification: 75 °C, 3.7 MPa CO, 10 h.
[b] Hydrogenation: 165 °C, 10.5 MPa H_2, 10 h.

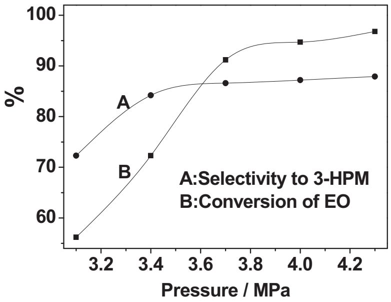


Fig. 2. Effect of CO pressure on hydroesterification of EO. $[Bmim]PF_6$ as solvent, Imidazole as promoter, 75 °C, 10 h.

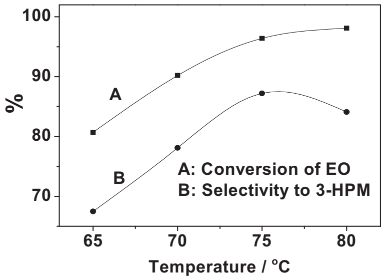


Fig. 3. Effect of temperature on hydroesterification of EO $[Bmim]PF_6$ as solvent, Imidazole as promoter, 3.7 MPa CO, 10 h.

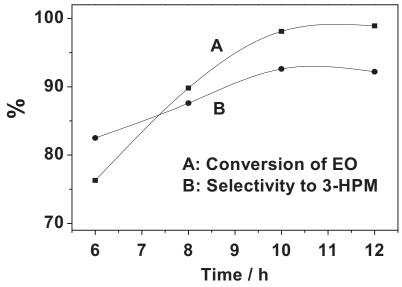


Fig. 4. Effect of time on hydroesterification of EO $[Bmim]PF_6$ as solvent, Imidazole as promoter, 75 °C, 3.7 MPa CO.

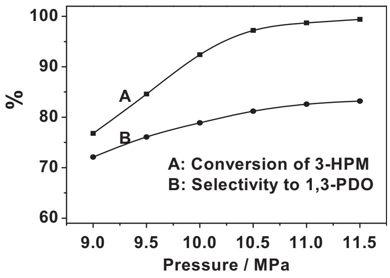


Fig. 5. Effect of H_2 pressure on hydrogenation of 3-HPM Imidazole as promoter, $[Bmim]PF_6$ as solvent. 165 °C, 10 h.

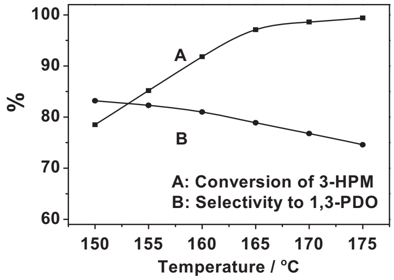


Fig. 6. Effect of temperature on hydrogenation of 3-HPM Imidazole as promoter, $[Bmim]PF_6$ as solvent. 10.5 MPa H_2, 10 h.

EO and activation of 3-HPM. The results are presented in Table 1 (entries 11–15).

3.7. Reaction conditions

Hydroesterification of EO was greatly influenced by the variation of pressure, temperature and reaction time (Figs. 2–4). The conversion of EO and the selectivity to 3-HPM increased with the increase of CO pressure, and was only a little change when CO pressure was more than 3.7 MPa. It seemed that the in situ formed active species were more stabilized and the inserted reaction of CO happened readily at higher pressures [26]. Upon increasing temperature and reaction time, the conversion of EO increased, but the selectivity to 3-HPM dropped off, because dehydration reaction of 3-HPM happened readily at higher temperature. The results indicated that the appropriate reaction conditions for hydroesterification of EO were 75 °C, 3.7 MPa CO and 10 h.

As seen in Figs. 5–7, the conversion of 3-HPM and the selectivity to 1,3-PDO increased with the increase of H_2 pressure. At higher temperature, dehydration reaction of 3-HPM happened readily, so the selectivity to 1,3-PDO decreased. The conversion of 3-HPM and the selectivity to 1,3-PDO increased with the increase of reaction time, but it was feeble when reaction time was more than 10 h.

3.8. Recovering and recycling of catalyst

Recycling performance of $[Bmim][Co(CO)_4]$ was investigated in $[Bmim]PF_6$ and using reaction conditions selected based on previous studies. The water phase, containing product and unconverted reactants, could be removed by simple phase decantation, the ionic liquid phase containing the catalyst could be recycled. Only very little amount of the catalyst (0.4–2.6%) leached into the water phase. Recycling experiments indicated good stability of the catalyst in the ionic liquid $[Bmim]PF_6$ with no significant loss in activity and selectivity during three consecutive runs. The recycling results were compiled in Table 2.

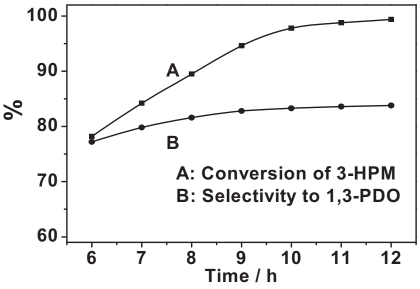


Fig. 7. Effect of reaction time on hydrogenation of 3-HPM Imidazole as promoter, $[Bmim]PF_6$ as solvent. 165 °C, 10.5 MPa.

Table 2
Recycling performance of [Bmim][Co(CO)$_4$][a].

Time	Hydroesterification[b]		Hydrogenation[c]	
	EO conversion (%)	Selectivity to 3-HPM(%)	3-HPM conversion (%)	Selectivity to 1,3-PDO(%)
1	98.1	92.6	99.2	83.6
2	94.3	90.5	95.3	80.5
3	88.9	90.2	90.7	78.6

[a] Imidazole as promoter, [Bmim]PF$_6$ as solvent.
[b] Hydroesterification: 75 °C, 3.7 MPa CO, 10 h.
[c] Hydrogenation: 165 °C, 10.5 MPa H$_2$, 10 h.

4. Conclusions

Using [Bmim][Co(CO)$_4$] as catalyst and [Bmim]PF$_6$ as solvent, 3-HPM was synthesized by hydroesterification of EO and 1,3-PDO was prepared successfully by hydrogenation of 3-HPM. Functional ionic liquid [Bmim][Co(CO)$_4$] was prepared by metathesis reaction between [Bmim]Cl and KCo(CO)$_4$and its structure had been illustrated by FT-IR and ^{1}H NMR.

Under a pressure of 3.7 MPa and at temperature of 75 °C, the conversion of EO can reach 98.1% and the selectivity to 3-HPM can reach 92.6%. Even after the catalyst is recycled three times, reaction yield still reached around 80%.

The appropriate reaction conditions of hydrogenation of 3-HPM were 165 °C, 10.5 MPa H$_2$ and 10 h. Under the optimum conditions, the best conversions of 3-HPM were up to 99.2% with selectivity in the 1,3-PDO up to 83.6%, the catalyst could be recycled three times with the yield of 1,3-PDO not less than 70%.

Acknowledgments

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