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Article

Synthesis of propylene glycol ethers from propylene oxide catalyzed by environmentally friendly ionic liquids

Cong Zhao ^{a,b}, Shengxin Chen ^{b,c}, Ruirui Zhang ^b, Zihang Li ^b, Ruixia Liu ^{b,#}, Baozeng Ren ^a, Suojiang Zhang ^{a,b,*}

^a School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, Henan, China

^b Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^c College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, Henan, China

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ABSTRACT

A series of acetate ionic liquids were synthesized using a typical two-step method. The ionic liquids were used as environmentally benign catalysts in the production of propylene glycol ethers from propylene oxide and alcohols under mild conditions. The basic strengths of the ionic liquids were evaluated by determination of their Hammett functions, obtained using ultraviolet-visible spectroscopy, and the relationship between their catalytic activities and basicities was established. The catalytic efficiencies of the ionic liquids were higher than that of the traditional basic catalyst NaOH. This can be attributed to the involvement of a novel reaction mechanism when these ionic liquids are used. A possible electrophilic-nucleophilic dual activation mechanism was proposed and confirmed using electrospray ionization quadrupole time-of-flight mass spectrometry. In addition, the effects of significant reaction parameters such as concentration of catalyst, molar ratio of alcohol to propylene oxide, reaction temperature, and steric hindrance of the alcohol were investigated in detail.

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1. Introduction

Ionic liquids (ILs) have become a hot research topic in recent years. They have been used extensively as catalysts and solvents in organic synthesis because of their negligible vapor pressures, high thermal stabilities, and reusability [1–3]. Functional ILs for specific purposes can be easily designed by adjusting the anion and cation [4]. Ring-opening reactions of epoxides have attracted widespread attention, especially cycloadditions with CO₂ [5–7] and alcohols [8] to produce prod-

ucts with various applications in environmental protection and economic development. ILs facilitate opening of the C–O bond in epoxides and can be used in the fixation of CO₂ with epoxides through hydrogen-bonding interactions [9–12].

There are several methods for producing propylene glycol ethers [13–15], among which the most commercially promising and industrially feasible method is the etherification of propylene oxide (PO), i.e., the reaction of PO with low-carbon alcohols over various catalysts. Propylene glycol ethers, mainly propylene glycol methyl ether, propylene glycol ethyl ether,

* Corresponding author. Tel/Fax: +86-10-82544875; E-mail: sjzhang@home.ipe.ac.cn

Corresponding author. Tel/Fax: +86-10-82544875; E-mail: rxliu@ipe.ac.cn

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and propylene glycol butyl ether, are fine chemicals with a range of applications because they contain an ether bond and hydroxyl group, which are hydrophobic and hydrophilic, respectively. Propylene glycol ether is an excellent solvent; it is referred to as an “alkahest” solvent and is widely used as a pollution-free solvent, e.g., for paints, inks, printing, electronic chemicals, dyes, leather, and textiles [16]. Most conventional homogeneous catalysts have disadvantages such as difficulty of separation, the need for liquid waste treatment, corrosion, and reusability problems. Heterogeneous catalysts have low efficiencies and are difficult to control. Much effort has therefore been made to develop novel effective catalysts [17–20].

Many highly active and selective base- and acid-containing homogeneous and heterogeneous catalysts have been used in the synthesis of propylene glycol ethers. Various homogeneous catalysts (NaOH [21], sodium alcoholates [22–24], amines [13], and hydroxides [25]) and heterogeneous catalysts (basic metal oxides such as MgO [17] and CaO [26], amine-modified porous silica [27,28], alumina-pillared clays [29], and molecular sieves [20,30]) have been widely used as basic catalysts. Homogeneous (BF₃ and H₂SO₄ [13]) and heterogeneous (Zr, Al-pillared clays [19], acidic zeolites [31], and acid-modified montmorillonite [32]) have also been investigated as acidic catalysts for this reaction. However, the mechanism of the alcoholysis of PO depends on the acid-base properties of the catalyst [33]. With basic catalysts, the C–O bond preferentially opens at the least sterically hindered position, resulting in predominant formation of the secondary alcohols 1-alkoxy-2-propanol (II, Scheme 1). In the presence of acidic catalysts, the secondary alcohols 2-alkoxy-1-propylene (I) are mainly obtained. In addition, both products can polymerize with PO to generate polyether polyols (III) as by-products, as shown in Scheme 1.

The primary alkyl ethers of propylene glycol are much more toxic than the secondary alkyl ethers [34,35]. Based on these factors, high selectivity for secondary alcohol ethers is desirable. Mechanistic studies have shown that the high selectivity for II in base-catalyzed reactions can be attributed to the dissociation of ROH to a proton and alkoxide species in the presence of basic sites of moderate strength and weak Lewis acid sites [36–38]. The key step in the reaction is the ring opening of PO by RO[−] (basic anion) under basic conditions [33]. However, the catalytic mechanism of ILs may differ from the traditional pathway because ILs can affect the process and efficiency of catalytic reactions via factors such as their solvation properties, interactions with substrates, and transition states [1].

Few ILs, except tetramethylguanidine-based ILs, have been studied as catalysts for the synthesis of propylene glycol ethers from PO and alcohols [39], despite their special effects on the reaction. In this work, a series of acetate ILs were prepared and characterized, and used as environmentally friendly and

non-halogen-functionalized basic IL catalysts in the synthesis of propylene glycol ethers from PO and low-carbon alcohols. The products of such reactions have high solubilities and low toxicities. They have a broad potential market as important raw materials and premium organic solvents in the fine chemical industry. The catalytic properties and basic strengths of various acetate ILs in this reaction were assessed and the relationships between these properties were investigated. 1-Ethyl-3-methylimidazolium (Emim)OAc was studied in detail, and its performance was compared with that of the conventional basic catalyst NaOH. The mechanism of the IL-catalyzed reaction was investigated and compared with that in the case of a traditional basic catalyst to clarify the reasons for the different catalytic features. The effects of important reaction parameters such as catalyst concentration, alcohol/PO molar ratio, reaction temperature, and alcohol structure were investigated systematically.

2. Experimental

2.1. Materials

PO, methanol, butanol (*n*-butanol, isobutanol, *sec*-butanol, and *tert*-butanol), lead acetate trihydrate, NaOH, and bromothymol blue (BTB) indicator were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *N*-methylimidazole and bromoethane were purchased from the Aladdin Reagent Co., Ltd. (Shanghai, China). All the chemicals were analytical reagent grade and used without further purification.

2.2. Synthesis and characterization of ILs

The ILs used in this work were prepared using a typical ion-exchange method involving two steps, namely quaternization and anion metathesis [40–43]. The general equations for the reactions involved in the synthesis of these ILs are shown in Scheme 2.

The chemical structures of these ILs were determined using nuclear magnetic resonance (NMR) spectroscopy. ¹H NMR spectra were recorded using a JNM-ECA-600 spectrometer (JEOL Ltd., Tokyo, Japan) with DMSO-*d*₆ as the solvent. Thermal gravimetric analysis (TGA) was performed using a TGA-Q5000 instrument (TA Instruments) in the temperature range 30–300 °C at a heating rate of 5 °C/min in a nitrogen atmosphere. The water contents of the ILs were determined using coulometric Karl Fischer titration (C20 Coulometric KF titrator, Mettler Toledo, OH, USA). Details of the IL synthesis are given below.

R₁, R₂, R, R': alkyl; X: halogen; M: Pb, Ag, NH₄, H, etc.

Scheme 2. Synthesis of acetate ILs using a two-step method.

Scheme 1. Reaction pathway for synthesis of propylene glycol ethers.

1-Ethyl-3-methylimidazolium bromide (EmimBr) was prepared by mixing *N*-methylimidazole with bromoethane at a molar ratio of 1:1.2 in a 250 mL three-necked, round-bottomed flask. The reaction was performed under ambient conditions with magnetic stirring for 4 h. A reflux condenser was connected to the flask to avoid volatilization of the reactants. The mixture components were separated by reduced pressure distillation and the resultant white solid was washed three times with ethyl acetate to remove the remaining feedstock and other impurities thoroughly. The obtained EmimBr was dried under high vacuum (–3 to 0 Pa) at 70 °C for 24 h with P₂O₅ as a desiccant. ¹H NMR (EmimBr, DMSO-*d*₆): 1.31 (t, 3H), 3.86 (m, 2H), 4.18 (s, 3H), 7.78 (d, 2H), 9.73 (s, H); purity: 99%.

BmimBr was prepared in a similar way using C₄H₉Br instead of bromoethane. ¹H NMR (BmimBr, DMSO-*d*₆): 0.92 (t, 3H), 1.25 (m, 2H), 1.77 (m, 2H), 3.88 (s, 3H), 4.20 (t, 2H), 7.84 (d, 2H), 9.29 (s, H); purity: 97%.

For the synthesis of 1-ethyl-3-methyl imidazole acetate (EmimOAc), EmimBr and lead acetate trihydrate were dissolved in deionized water at a molar ratio of about 2:1. The EmimBr solution was added dropwise to the lead acetate solution under stirring at room temperature for 4 h. After precipitation, the mixture was transferred to a refrigerator and left for 5 h for sedimentation. The filtrate was obtained by vacuum filtration while the mixture was still cool. The drying and purification procedure described above was used. Bright-yellow viscous EmimOAc was obtained and stored in a desiccator. ¹H NMR (DMSO-*d*₆): 1.31 (t, 3H), 1.59 (s, 3H), 3.86 (s, 3H), 4.18 (m, 2H), 7.74 (s, H), 7.83 (s, H), 9.73 (s, H); decomposed 180 °C; purity: 98%.

Other acetate ILs, namely DmimOAc, BmimOAc, and N₂₂₂₂OAc, were synthesized using similar methods; the structures of the ILs are shown in Scheme 3. ¹H NMR (BmimOAc, DMSO-*d*₆): 0.88 (t, 3H), 1.23 (m, 2H), 1.57 (s, 3H), 1.75 (m, 2H), 3.88 (s, 3H), 4.19 (t, 2H), 7.84 (d, 2H), 10.06 (s, H); purity: 98%. ¹H NMR (DmimOAc, DMSO-*d*₆): 0.84 (t, 3H), 1.23 (s, 15H), 1.56 (s, 3H), 1.76 (m, 2H), 3.87 (s, 3H), 4.18 (t, 2H), 7.81 (d, 2H), 9.99 (s, H); purity: 97%. ¹H NMR (N₂₂₂₂OAc, DMSO-*d*₆): 1.15 (t, 12H), 1.54 (s, 3H), 3.22 (m, 8H); purity: 98%.

2.3. Basicity measurements

The basic strengths of the ILs and conventional NaOH catalyst used in the experiments were evaluated based on their Hammett functions. These were determined using ultraviolet-visible (UV-vis) spectroscopy [44] by evaluating the deprotonation extent of an indicator (HI) based on the measured

ratio [HI]/[I[–]]. [HI] is the concentration of the protonated form and [I[–]] is the concentration of the deprotonated form.

For dissociation in a specific solvent, the Hammett function (*H*₀) is defined as *H*₀ = p*K*(HI)_{al} + log([I[–]]_s/[HI]_s), where p*K*(HI)_{al} is the p*K*_a value of the indicator in a given alcoholic solution.

BTB was chosen as the indicator and methanol was used as the solvent because alcohols were reagents in the alcoholysis reaction. The test solutions were prepared by mixing the catalyst (0.01 mol/L) and BTB (1.6 × 10^{–5} mol/L) with methanol. The highest absorbance of the unprotonated form of the BTB at 620 nm was determined at NaOH concentrations of 0.1 and 0.01 mol/L. The [I[–]]/[HI] ratio was obtained from the absorbance, and *H*₀ was calculated based on the Hammett function of the unprotonated form of the indicator.

2.4. Catalytic performance tests

Reactions were performed in a stainless-steel autoclave reactor of inner volume 100 mL. A typical procedure was as follows. PO and *n*-butanol in molar ratios of 1–10 and a certain amount of catalyst were introduced into the autoclave. After running the reaction at 80–140 °C for 30–240 min under magnetic stirring, the reactor was cooled to room temperature to give the target products.

The mixtures after reaction were analyzed using a gas chromatography (GC) system (Shimadzu GC-2010 plus) with a flame ionization detector and a capillary column (HP-INNOWax), combined with electrospray quadrupole time-of-flight mass spectrometry (ESI-QTOF-MS; Bruker QTOF II); mass spectrometric “negative ion fishing” was used [45].

The reusability of the IL catalysts was also investigated, using EmimOAc as an example. The recycling of EmimOAc used in the synthesis of propylene glycol butyl ether at 100 °C for 30 min was investigated. After the reaction, the products and excess reactants were removed and the IL catalyst was separated from the reaction mixture by vacuum distillation and dried at 70 °C for more than 5 h for reuse. The structure and purity of the recovered EmimOAc were checked using ¹H NMR spectroscopy.

3. Results and discussion

3.1. Catalytic performance of various ILs

A series of acetate-based ILs, i.e., DmimOAc, BmimOAc, EmimOAc, and N₂₂₂₂OAc, were used in the synthesis of propylene glycol butyl ether from PO and *n*-butanol. The conventional catalyst NaOH and the halogen-containing IL BmimBr were also studied for comparison. The catalytic reaction results are shown in Fig. 1. The conversion decreased in the sequence DmimOAc (93.94%) > BmimOAc > EmimOAc > NaOH > N₂₂₂₂OAc > BmimBr. The cation in DmimOAc, BmimOAc, and EmimOAc had little effect on the conversion. Similar conversions were obtained with these three catalysts, and the conversions were more than ~30% and ~85% higher than those achieved with NaOH and BmimBr (3.93%), respectively. Among all the catalysts investigated, N₂₂₂₂OAc gave the best

Scheme 3. IL catalysts used in the present work.

Fig. 1. Performances of various catalysts in synthesis of propylene glycol butyl ether from PO and *n*-butanol. Reaction conditions: PO 0.1 mol, *n*-butanol 0.3 mol, catalyst 0.2 mmol, 2 h, 120 °C.

selectivity for II (94.4%), followed by NaOH, BmimBr, and the imidazolium acetate-based ILs, which gave similar selectivities. These results suggest that the catalytic performance was related to the catalyst properties and structure.

The basic strength of a catalyst strongly affects its activity and selectivity in the synthesis of propylene glycol ethers [30]. The catalytic performances of the various different catalysts were investigated by determining their basic strengths and exploring the correlation between catalytic properties and basicity.

The UV-vis spectrum of the BTB indicator ($pK(HI)_{al} = 12.4$) for a specific catalyst concentration was recorded and the basic strength was evaluated by determination of the Hammett function [44]; the results are listed in Table 1. The data in Table 1 show that the order of the basic strengths was NaOH > BmimOAc > DmimOAc > EmimOAc > N₂₂₂₂OAc > BmimBr. NaOH is a strong base and the H_0 is 13.57 at a concentration of 0.001 mol/L in methanolic solution. The basic strengths of BmimOAc and DmimOAc were approximately equivalent, 11.47 and 11.42, respectively; they are therefore weaker bases than NaOH and slightly stronger than EmimOAc. The basic strengths of the different imidazolium acetate-based ILs, which are affected mainly by the cation-anion interaction energy [46] and hydrogen-bond donor ability [47], according to density functional theory calculations, are in good agreement with those reported in the literature. The basicity of an acetate IL with an

Table 1

Basic strengths of various catalysts determined from Hammett functions.

Catalyst	C_{CAT} (mol/L)	A_{max}	[I] (%)	[HI] (%)	H_0 (± 0.05)
NaOH	0.01	1.779	100	0	—
NaOH	0.001	1.666	93.65	6.35	13.57
BmimOAc	0.01	0.188	10.57	89.43	11.47
DmimOAc	0.01	0.170	9.56	90.44	11.42
EmimOAc	0.01	0.116	6.52	93.48	11.24
N ₂₂₂₂ OAc	0.01	0.097	5.45	94.55	11.16
BmimBr	0.01	0.0004	0.02	99.98	8.75

imidazolium cation is stronger than that of an IL with a quaternary ammonium cation because of the electrophilic inductive effects of the counter cations [48] and solvent effects. The basicity of the halogen-containing IL BmimBr was extremely weak, which highlights the effect of the anion on the IL basicity.

For the catalysts investigated, the relationship between yield and basicity was not straightforward, as shown in Fig. 2. It is worth mentioning that in comparisons of the basicities and yields achieved using IL catalysts and NaOH, the basic strength may not be the dominant factor. Furthermore, BmimOAc is a stronger base than DmimOAc, but their yields of II suggest the opposite trend; this might be because of the strong dissolving capacity of DmimOAc resulting from the long alkyl chains in the imidazolium-based cation. The inferior catalytic efficiency (~27% conversion) of N₂₂₂₂OAc is attributed to a poor ability to open the ring and form the corresponding intermediates because of the absence of the C-2 hydrogen in imidazolium-based ILs [49].

The results suggest that the catalytic efficiencies of ILs are not only related to the anions, and the counter cations also play an important part in molecular-level interactions during the catalytic process. Here, we chose EmimOAc as a probe catalyst and further investigated the catalytic features of these environmentally benign halogen-free IL catalysts in the synthesis of propylene glycol ethers from PO and alcohols.

3.2. Catalytic features of acetate IL catalysts

3.2.1. Comparison of catalytic performance of acetate ILs with that of NaOH

The catalytic performance of EmimOAc in the synthesis of propylene glycol butyl ether from PO and *n*-butanol were investigated at *n*-butanol:PO molar ratios of 1 and 3 and various EmimOAc concentrations, and compared with that of NaOH. Fig. 3(a-1) shows that the PO conversions increased from 77.4% to 98.2% and 83.3% to 91.1% at an EmimOAc concentration of 14.5 mmol/L when the reaction time was increased from 30 to 240 min; these are higher than the conversions with NaOH, which increased from 39.7% to 93.7% and 34.0% to 81.5% under the same conditions. The PO conversions and

Fig. 2. Relationship between yields of II (Scheme 1) and basic strengths of various IL catalysts. Reaction conditions: PO 0.1 mol, *n*-butanol 0.3 mol, EmimOAc 0.2 mmol, 2 h, 120 °C.

selectivities for II were both higher with EmimOAc than with NaOH at both *n*-butanol/PO molar ratios in 240 min, even at high conversions. Here, the catalytic tests were performed at low molar ratios of alcohol:PO for atom economy; in industrial applications, ratios of 10 to 16 are commonly used [19,29]. The selectivity of EmimOAc (Fig. 3(b-1)) for II was initially lower than that of NaOH, but it decreased more slowly with time and became almost constant in this cascade reaction. The selectivities decreased from 87.9% to 84.6% with EmimOAc and 91.4% to 81.3% with NaOH for an *n*-butanol/PO molar ratio of 3, and from 68.3% to 64.7% with EmimOAc and 85.3% to 63.6% with NaOH for an *n*-butanol/PO ratio of 1, for reaction times from 30 to 240 min. These results show that a higher selectivity for II was obtained with EmimOAc even at low alcohol/PO molar ratios, and further etherification of II to III was suppressed in this cascade reaction compared with the reaction with NaOH. A much bigger difference between the PO conversions at *n*-butanol/PO ratios of 1 and 3 with EmimOAc at a lower catalyst concentration of 5.8 mmol/L compared with the conversion using NaOH was observed, as shown in Fig. 3(a-2) and (b-2). For EmimOAc, the PO conversions were about 30% and 20% higher than those achieved with NaOH at *n*-butanol/PO molar ratios of 3 and 1 in 240 min; the differences between the selectivities for II were smaller.

3.2.2. Mechanism of reaction catalyzed by EmimOAc

The above results show that there are observable differences between the catalytic properties of the acetate IL catalysts and the conventional basic catalyst NaOH. Different reaction mechanisms are assumed to be responsible for the discrepancy between the catalytic performances. Traditional basic catalysts such as NaOH, sodium alcoholates, and amines (C_nH_{2n+1})₃N for the alcoholysis of PO have been studied for decades [33]. It is generally considered that these catalysts work as follows. The alcohol readily dissociates to an electron-donating alkoxide and a proton on the active centers of the catalyst. The active sites coordinate with PO to generate propylene-like species via carbanion intermediates formed by simultaneous electron withdrawal and ring opening. The alkoxide reacts with the propylene-like species in an anti-Markownikov fashion, leading to the formation of a 1-alkoxy-2-propanol anion via addition. The target products are obtained by proton capture. The ring opening of PO by RO⁻ derived from an alcohol in the presence of a basic catalyst is considered to be the critical step [9]. ILs could also be involved in a similar pathway, as shown in Scheme 4, path (b). In this catalytic route, butanol is deprotonated by the acetate IL to produce butoxy species and the alcohol ether is formed by etherification of PO and the butoxy species by cycloaddition.

Fig. 3. Comparison of catalytic performance of EmimOAc and NaOH in synthesis of propylene glycol ether from PO and *n*-butanol. Reaction conditions: V_{total} 34.4 mL, 120 °C.

Scheme 4. Proposed mechanism of synthesis of propylene glycol ether from PO and *n*-butanol catalyzed by EmimOAc.

An electrophilic-nucleophilic dual activation mechanism is proposed for synthesis of propylene glycol ether from PO and butanol using acetate IL catalysts. The ILs are thought to facilitate ring opening based on the drag effect of hydrogen-bonding interactions between anions and cations on PO. Electrophilic and nucleophilic catalysis of hydrogen bonding in the reaction was investigated and hydrogen bond clusters were successfully detected using MS.

Direct evidence of relevant reactive intermediates was obtained by MS analysis of aliquots of sample withdrawn before and after the reaction in the presence of EmimOAc. The ion peaks of the corresponding hydrogen-bonded clusters or reactive intermediates were observed. Ions at m/z 59.01, 117.05, and 133.09 corresponding to $[\text{AcO}^-]$, $[\text{AcO}^- + \text{PO}]$, and $[\text{AcO}^- + \text{BuOH}]$, respectively, were observed (Fig. 4). This indicates that the $[\text{AcO}^-]$ anion of the IL was involved in the formation of $[\text{A}_1]$ and $[\text{A}_2]$ (Scheme 4). The characteristic ion peaks at 191.13 and 249.17, corresponding to $[\text{PO} + \text{AcO}^- + \text{BuOH}]$ and $[2\text{PO} + \text{AcO}^- + \text{BuOH}]$, respectively, were consistent with the formation of the target product II and by-product III. The reactive intermediate of propylene glycol ether, $[\text{PO} + \text{AcO}^- + \text{BuOH}]$, provided evidence of hydrogen-bonding and charge-charge interactions to form $[\text{B}_1]$ and $[\text{B}_2]$ (Scheme 4). A combination of the experimental results for catalysis using various ILs suggests that the catalytic efficiency of the IL is not solely related to the AcO^- anion, and the cation also plays an important part in the molec-

ular-level interactions during catalysis. This supports the proposed electrophilic-nucleophilic dual activation mechanism in the catalytic process. The better hydrogen-bond donor ability of the imidazolium cation leads to the formation of the five-membered hydrogen-bonded cluster $[\text{B}_1]$ and makes imidazolium-based acetate ILs more effective than conventional catalysts that do not have good hydrogen-bond donors. Furthermore, the corresponding anion $[\text{PO} + \text{OAc}^- + \text{BuOH}]$ was also detected, which proves the validity of our conjecture.

The acetate ILs are assumed to participate in electrophilic-nucleophilic dual activation through cooperative hydrogen-bonding and charge-charge interactions in which the cationic moiety acts as an electrophilic attacker and the anion acts as a nucleophilic attacker. Based on the proposed electrophilic-nucleophilic dual activation mechanism, strong basicity and nucleophilic ability can facilitate ring opening of PO and deprotonation of alcohols, leading to the formation of intermediate species; this provides a rationale for the observed activities in the presence of various ILs. Such dual activation was also found in *o*-*tert*-butoxycarbonylation of 2-naphthol with Boc_2O catalyzed by BmimOAc [49].

The recovery and reuse of catalysts is of great importance for the chemical industry for economic and environmental reasons. Compared with NaOH, IL catalysts have excellent recycling potential because they are non-volatile and thermally stable. As an example, the recycling of EmimOAc was evaluated in the synthesis of propylene glycol butyl ether at 100 °C for 30 min. After the reaction, the products and excess reactants were removed and then the IL catalyst was separated from reaction mixture by vacuum distillation. For the recycled catalyst, the conversion decreased slightly in the initial cycle and decreased greatly in the third run; the selectivity for diether at the expense of the main product II increased with the number of cycles. This was caused by significant accumulation of the heavier diether and polyether fraction, which is difficult to remove because of its high boiling point and strong solubility, leading to a decrease in the number of active centers and a poorer catalytic performance. This was confirmed by the ^1H NMR spectra of EmimOAc after recycling.

Fig. 4. ESI-QTOF-MS of negative ion sample of reaction mixture of PO and *n*-butanol in the presence of EmimOAc.

3.3. Optimization of reaction parameters

3.3.1. Effect of different alcohols

The EmimOAc-catalyzed etherifications of PO with different alcohols at 120 °C for 2 h were examined. The results (Fig. 5) show that the alcohol structure plays a significant role in the reactivity and product distribution. In terms of carbon chain length, the conversion of PO decreased in the order methanol > ethanol > butanol, which suggests that shorter alkyl chains give higher conversions. In terms of branched structures, the conversion decreased in the order *n*-butanol > isobutanol > *sec*-butanol > *tert*-butanol; this can be attributed to the position of the hydroxyl group reacting with PO in the etherification. Similar conclusions have been reported for other reactions such as resin-catalyzed alcoholysis of epoxidized fatty esters [50]. Possible reasons are as follows. First, the epoxide ring-opening rate decreases with increasing number of branches and size of the alcohol because of the higher steric hindrance imposed by the branches and carbon chains. Furthermore, the charge effect of RO⁻ derived from isobutanol by deprotonation is stronger than those of alkoxy groups derived from *sec*-butanol and *tert*-butanol because of the different positions of the hydroxyl group. The charge effect of alkoxy weakens on transfer of hydroxyl groups to secondary carbons and tertiary carbons, leading to significant decreases in activity because of the different ring-opening abilities of RO⁻. This implies that the alcohol structure alters the charge effect of the alkoxy group, and this affects the catalytic performances and ring-opening abilities of different RO⁻ groups. In addition, the melting points of alcohols such as *tert*-butanol, which are relatively high because of phase changes, also make alcoholysis more difficult.

3.3.2. Effect of catalyst concentration

The effect of catalyst concentration was studied in the range 0.1–1 mol% relative to PO; the results are shown in Fig. 6. The conversion and selectivity strongly depended on the catalyst concentration. The PO conversion increased sharply with increasing EmimOAc concentration, whereas the selectivity for II

Fig. 5. Results of etherification of PO with different alcohols catalyzed by EmimOAc. Reaction conditions: EmimOAc 5.8 mmol/L, V_{total} 34.4 mL, 2 h, 120 °C.

decreased slightly. The highest conversion was 98.2%, for catalyst addition of 1 mol% and 240 min; the corresponding selectivity for II was 84.5%. This is because the high number of active centers and basic sites provided for the catalytic reaction gives the reactants more efficient access to the active catalytic sites, resulting in increased production of propylene glycol butyl ether. However, the increase in the quantity of the target product, i.e., propylene glycol monobutyl ether, increased side reactions, leading to the accumulation of by-products and a corresponding decline in selectivity. When the amount of catalyst exceeded 0.3 mol% (molar ratio of catalyst to PO), there were no obvious changes in the conversion and selectivity, which suggests that the amount of catalyst was no longer a limiting factor in the reaction. At a given catalyst concentration, the PO conversion increased over time, but the selectivity decreased. However, the conversion and selectivity were both stable after a certain period of time, possibly because the reaction was complete.

3.3.3. Effect of *n*-butanol/PO molar ratio

The effects of different *n*-butanol/PO molar ratios at con-

Fig. 6. Effect of EmimOAc concentration. Reaction conditions: PO 0.1 mol, *n*-butanol 0.3 mol, 120 °C.

stant PO concentration and constant volume on the reaction were studied. Fig. 7 shows that the conversion and selectivity in PO alcoholysis varied significantly with increasing molar ratio of *n*-butanol/PO; the selectivity for II increased continuously, with a maximum selectivity greater than 94% for both conditions. The PO conversion initially increased and then decreased; a maximum conversion of 88.6% under condition (a) and 68.4% under condition (b) were obtained at *n*-butanol/PO molar ratios from 1 to 10. This indicates that the concentrations of the reactants and catalyst significantly affect the reaction. This is because increasing the number of effective collisions between reactants and catalyst molecules increases the opportunity for intermolecular contacts, and this improves the PO conversion and selectivity for II, depending on the *n*-butanol/PO molar ratio. When the amount of alcohol is increased, the amount of PO is relatively small, which makes it difficult to access PO molecules and reduces the probability of dimeric and polymeric reactions, resulting in a continual increase in the selectivity. When the feed ratio of *n*-butanol to PO was greater than 3:1, the PO conversion did not increase further and began to decrease; this is because of dilution of the reaction system caused by adding a large amount of *n*-butanol. When excess *n*-butanol is used, the number of collisions between the reactants and catalyst is reduced, resulting in decreased activity. A comparison of the results obtained using an equimolar amount of PO (Fig. 7(b)) with those using a constant concentration of EmimOAc and reaction volume (Fig. 7(a)) shows that the trends in the conversion and selectivity were similar, but the value of the conversion changed significantly because of the decreasing concentration of EmimOAc with increasing volume of the reaction system under condition (b).

3.3.4. Effect of reaction temperature

The dependences of the PO conversion and selectivity for II on reaction temperature in the reactions catalyzed by EmimOAc and NaOH were investigated. For EmimOAc, the curve representing changes in PO conversion was parabolic. Within the temperature range studied, the PO conversion first increased with increasing temperature from 100 to 140 °C, and then decreased with increasing reaction temperature up to

160 °C. Fig. 8 shows that the selectivity for the target product II dropped slightly with increasing temperature from 100 to 150 °C, and then declined sharply at temperatures higher than 150 °C. For the NaOH catalyst, the PO conversion increased with increasing temperature from 100 to 160 °C, but then remained steady during further temperature increases. The trend in the selectivity of the NaOH-catalyzed reaction with increasing temperature was the same way as that for the EmimOAc-catalyzed reaction. At the optimum temperatures, i.e., 140 °C for the EmimOAc-catalyzed reaction and 160 °C for the NaOH-catalyzed reaction, the PO conversions were 96.5% and 90.5%, respectively. Enhanced deprotonation and poorer ring-opening abilities could explain the increases and decreases in the catalytic performance in the presence of NaOH and EmimOAc with increasing temperature [51].

4. Conclusions

A series of acetate ILs were prepared and used as efficient and environmentally benign catalysts for the synthesis of propylene glycol ethers from PO and alcohols. The catalytic activity increased with increasing catalyst basicity for catalysts with moderate basic strengths because of generation of alkoxide and carbanion intermediates. The reaction system was extended to different alcohols, and the results showed that the catalytic properties were associated with the alcohol structure; shorter carbon chains and fewer branched chains gave better activities because of decreased steric hindrance. The catalytic performance of the acetate ILs was better than that of the traditional catalyst NaOH under the same reaction conditions. A mechanism different from that for traditional basic catalysts, namely an electrophilic-nucleophilic dual activation mechanism, involving cooperative hydrogen-bonding and charge-charge interactions, was proposed. The cationic moiety is assumed to act as an electrophilic attacker, and the anion acts as a nucleophilic attacker. The mechanism was verified using ESI-QTOF-MS, which showed that direct activation of PO by the IL effectively promoted formation of the target product and prevented the formation of by-products in this cascade reaction. Optimization of the reaction conditions showed that the catalytic perfor-

Fig. 7. Effect of *n*-butanol/PO molar ratio at constant volume and catalyst concentration (a) and constant number of moles of PO and catalyst (b). Reaction conditions: (a) EmimOAc 5.8 mmol/L, V_{total} 34.4 mL, 2 h, 120 °C; (b) PO 0.1 mol, 2 h, EmimOAc 0.2 mmol, 120 °C.

Fig. 8. Effect of temperature in etherification of PO and *n*-butanol catalyzed by EmimOAc (a) and NaOH (b). Reaction conditions: PO 0.1 mol, *n*-butanol 0.3 mol, catalyst 0.2 mmol, 2 h.

mance improved with increasing catalyst concentration, and a conversion and selectivity of 98.2% and 86.4% were achieved when the catalyst concentration was 1% (molar ratio of catalyst and PO). The optimum molar ratio of alcohol to PO was about 3, and the optimum temperature was about 140 °C.

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Graphical Abstract

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Synthesis of propylene glycol ethers from propylene oxide catalyzed by environmentally friendly ionic liquids

Cong Zhao, Shengxin Chen, Ruirui Zhang, Zihang Li, Ruixia Liu *,
 Baozeng Ren, Suojiang Zhang *
 Zhengzhou University;
 Institute of Process Engineering, Chinese Academy of Sciences;
 Henan University

Propylene glycol ethers, namely propylene glycol methyl ether, propylene glycol ethyl ether, and propylene glycol butyl ether, were synthesized from propylene oxide and alcohols using a green process catalyzed by environmentally benign ionic liquids.

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环境友好型离子液体催化环氧丙烷反应合成丙二醇醚

赵 聪^{a,b}, 陈圣新^{b,c}, 张瑞锐^b, 李自航^b, 刘瑞霞^{b, #}, 任保增^b, 张锁江^{a,b,*}

^a郑州大学化工与能源学院, 河南郑州450001

^b中国科学院过程工程研究所离子液体与绿色工程研究部, 北京100190

^c河南大学化学与化工学院, 河南开封475004

摘要: 丙二醇醚类化合物是性能优良的精细化学品, 也是环保型高级溶剂. 该类化合物具有两个强溶解性功能基团—醚键和羟基, 前者具有亲油性, 可溶解疏水性物质, 后者具有亲水性, 可溶解亲水性物质, 因而丙二醇醚具有很强的溶解能力, 素有“万能溶剂”之称, 可广泛应用于涂料、油墨、油漆、印刷、电子化学品、染料、净洗和纺织等行业. 丙二醇醚类化合物目前主要由环氧丙烷和低级脂肪醇反应合成, 然而, 由于环氧丙烷的位阻效应, 使其在酸或碱的条件下开环的位置会不同, 从而得到不同的醇醚产物. 由于碱催化的醇醚产物更加环境友好, 因而越来越被人们所关注. 工业上丙二醇醚合成多采用传统的强碱性催化剂醇钠以及氢氧化钠, 腐蚀性强, 产生的废液量大. 本文采用环境友好的非卤素离子液体作为催化剂, 研究了其催化环氧丙烷醚化合成丙二醇醚的反应特性.

本文采用两步法合成了一系列环境友好的醋酸类碱性功能化离子液体, 并在温和的条件下将其用于催化环氧丙烷与醇反应合成丙二醇醚. 结果表明, 该类离子液体可以高效催化该反应的进行. 利用紫外-可见光谱测定Hammett指数来表征实验中所用离子液体的碱强度, 并构建了离子液体碱性与催化活性之间的关系. 结果表明, 离子液体的催化性能和其碱性密切相关, 随着离子液体碱性的增加, 催化活性增强, 其中咪唑醋酸类离子液体碱性强于季胺类, 表现出优异的催化性能. 离子液体的碱性明显弱于NaOH, 但却呈现出更优异的催化性能. 相同反应条件下, EmimOAc离子液体作为催化剂, PO的转化率分别较NaOH高出20%–30%, 选择性略高于NaOH, 这可能是由于二者催化机理不同造成的. 传统NaOH催化机理的关键步骤是醇在碱性催化剂的作用下去质子化形成电子供体烷氧根离子, 促进环氧丙烷的开环加成. 而本文提出了离子液体亲电亲核双活化作用机理, 即离子液体在阴阳离子之间的氢键和电荷相互作用的共同作用下, 促进环氧丙烷开环和醇的去质子化, 形成相应的反应中间体. 通过电喷雾质谱分析手段检测到了阴阳离子通过协同作用亲电亲核催化过程中的

反应中间体, 证明了该假设机理的可行性.

此外, 还考察了催化剂浓度、醇比、反应温度以及醇的空间位阻效应对反应的影响. 以EmimOAc催化合成丙二醇丁醚为例, 反应的转化率随催化剂浓度的增加而增大, 在催化剂添加量1% (催化剂与PO的摩尔比)时, PO转化率达到最大值为98.2%, 1-丁氧基-2-丙醇的选择性为86.4%. 当正丁醇与环氧丙烷的摩尔比为3时, 转化率最高为88.6%, 选择性高达94%. 该反应为放热反应, 最适反应温度约为140 °C, 此时转化率高达96.5%. 在环氧丙烷和不同的低碳醇合成丙二醇醚的反应中, 反应物醇的碳链越短, 支链越少, 催化反应效率越高.

关键词: 离子液体; 丙二醇醚; 酯化反应; 环氧丙烷; 碱强度; 反应机理; 环境友好

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*通讯联系人. 电话/传真: (010)82544875; 电子信箱: sjzhang@home.ipe.ac.cn

#通讯联系人. 电话/传真: (010)82544875; 电子信箱: rxliu@ipe.ac.cn

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