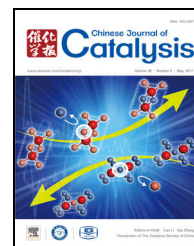


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

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

ARTICLE INFO

Article history:

Received 16 February 2017

Accepted 31 March 2017

Published 5 May 2017

Keywords:

Ionic liquid

Propylene glycol ether

Etherification

Propylene oxide

Basic strength

Reaction mechanism

Environmental friendly

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.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
Published by Elsevier B.V. All rights reserved.

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

This work was supported by the One Hundred Talent Program of CAS, the National Natural Science Foundation of China Petroleum & Chemical Corporation Joint Fund (U1662129), the National Natural Science Foundation of China (91434203), and the Key Research Program of Frontier Sciences, Chinese Academy of Sciences (QYZDY-SSW-JSC011).

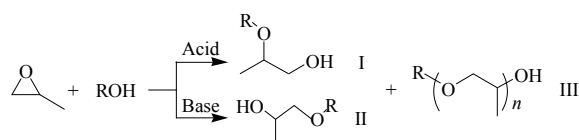
DOI: 10.1016/S1872-2067(17)62831-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 38, No. 5, May 2017

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



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

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

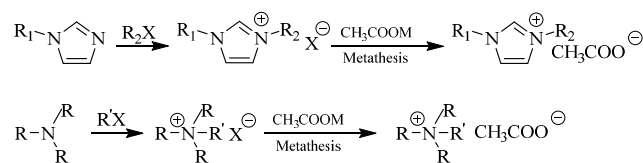
2.1. Materials

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.

Download English Version:

<https://daneshyari.com/en/article/6505927>

Download Persian Version:

<https://daneshyari.com/article/6505927>

[Daneshyari.com](https://daneshyari.com)