



Synthesis of glycerol carbonate from urea and glycerol using polymer-supported metal containing ionic liquid catalysts

Dong-Woo Kim, Kyung-Ah Park, Min-Ji Kim, Dong-Heon Kang, Jeong-Gyu Yang, Dae-Won Park*

School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea

ARTICLE INFO

Article history:

Received 1 November 2013
Received in revised form
11 December 2013
Accepted 23 December 2013
Available online 3 January 2014

Keywords:

Glycerol carbonate
Glycerol
Urea
Polymer support
Ionic liquid

ABSTRACT

Polystyrene-supported, metal containing imidazolium salt [PS-(Im)₂MX₂] catalysts were prepared and characterized by various analytical methods, and their role in the synthesis of glycerol carbonate from glycerol and urea was investigated under mild conditions. Among different metal containing PS-(Im)₂MBr₂ catalysts, the yield of GC increased Cu < Mg < Zn, which is the order of acid–base balance of the catalysts. PS-(Im)₂ZnI₂ catalyst, which showed a good balance of the acid–base properties, was the most active and selective catalyst; it was readily recoverable and reusable in the subsequent reaction cycles. Furthermore, the reaction pathway for the glycerolysis of urea was studied with the time-on-line analysis of the products *via* a combination of FT-IR spectroscopy and ¹³C NMR analysis. The effects of reaction parameters such as temperature, degree of vacuum, catalyst loading, and the ratio of reactants on the reactivity were also investigated to elucidate the reaction mechanism.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Since the last decade, biodiesel has gained increasing importance as a diesel-engine fuel for because it is renewable and clean [1–3]. Because of the rapid increase in the use of biodiesel and the sharp decrease in the price of glycerol (a by-product generated with the amount at one tenth of biodiesel production), glycerol can become a major platform chemical and has been identified as an important building block for future biorefineries by the DOE [4].

Among the chemicals derived from glycerol, glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one; GC) has been relatively recently introduced to the chemical industry and has been recognized to have extensive potential applicability [5–9]. Moreover, inexpensive GC could serve as a source of new polymeric materials such as glycidol, which is a high-value component in the production of a number of polymers [9,10]. The high functionality of glycidol, along with the versatile and well-investigated reactivity of its hydroxyl groups, has led to the formation of a number of derivatives. Indeed, many polyglycerols have been commercialized for applications ranging from cosmetics to controlled drug release [11].

GC is conventionally synthesized *via* typical protocols used for other low-molecular-weight organic carbonates. Transesterification of glycerol can be readily performed with dimethyl carbonate

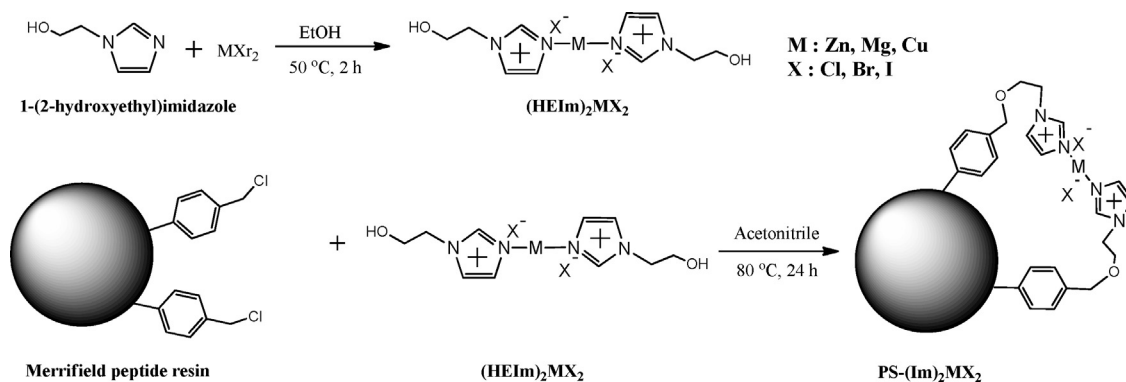
[12], ethylene carbonate [13], or propylene carbonate [14]. The carbonates utilized during the transesterification process are typically generated by utilizing phosgene or by means of energy-intensive routes employing epoxides. However, the reaction of glycerol with phosgene is limited by the toxic and environmentally hazardous nature of phosgene. Although there are some reports on the direct carbonylation of glycerol with carbon dioxide using tin complexes, the applicability of such processes is hampered by serious limitations such as unfavorable thermodynamic equilibrium and low yields [15].

An alternative synthesis method for GC is the glycerolysis of urea, a reaction that has been recently developed [16–18]. Its main advantage is that the reactants, glycerol and urea, are inexpensive, easily available, and neither explosive nor poisonous. In addition, the ammonia generated in the synthesis of GC from urea and glycerol can easily be converted back to urea by reaction with carbon dioxide.

Much effort has been devoted to the search for effective catalysts for the glycerolysis of urea. Homogeneous catalysis employing inorganic salts such as ZnSO₄ [19], MgSO₄ [20], and ZnO [21] has been described, and recently, certain heterogeneous systems based on these oxides have also been reported [22,23].

Polymer-supported catalysts are extensively used in both industry and academia because of the advantages they offer compared to homogeneous catalysts [24–26]. Recently, polymer-supported ionic liquids have been exploited as heterogeneous catalysts in the synthesis of cyclic carbonates, and were found to offer the dual

* Corresponding author. Tel.: +82 51 510 2399; fax: +82 51 512 8563.
E-mail address: dwpark@pusan.ac.kr (D.-W. Park).



Scheme 1. Preparation of polystyrene-supported metal containing imidazolium salt catalyst.

features of a homogeneous ionic liquid and heterogeneous catalyst. Compared to pure ILs, such heterogeneous catalysts have additional advantages such as facilitating the reduction of the amount of ILs employed, recovery of the catalyst from the reaction mixture, and ease of separation [27–29].

These data and the results of other prior studies [30,31] suggest that the catalysts for the reaction between glycerol and urea should possess both acidity and basicity to be effective, and also that there is a subtle balance between the acidity and basicity of such catalysts. In particular, the Lewis-acid sites activate the carbonyl group of urea whereas the Lewis-base sites activate the hydroxyl groups of glycerol [13,16,32].

In our previous work [33], the glycerolysis of urea was evaluated using metal containing ionic liquid (MIL) as efficient catalyst. However, the homogeneous system of MIL catalysts showed poor catalyst separation. The exploration of heterogeneous catalysts that are highly efficient under mild reaction conditions still remains a challenge. This paper reports the preparation of structurally modified polystyrene based on a Merrifield peptide resin supported metal containing imidazolium salt [PS-(Im)₂MX₂] and its characterization *via* various physicochemical methods. The catalytic performance of PS-(Im)₂MX₂ in the synthesis of GC from glycerol and urea is investigated. To improve the understanding of the reaction pathway and mechanism, the influence of the acid–base properties of the PS-(Im)₂MX₂ catalyst on the synthesis of GC is evaluated. In addition, the effects of the reaction time, reaction temperature, degree of vacuum, and catalyst loading are discussed. The PS-(Im)₂MX₂ catalyst was subjected to a recycle test in order to examine its stability.

2. Experimental

2.1. Materials

High-purity (>99%) 1-(2-hydroxyethyl)imidazole, metal halides (ZnCl₂, ZnBr₂, ZnI₂, MgBr₂, and CuBr₂), and Merrifield's peptide resin (MPR, 1% divinylbenzene, 4.0 mmol Cl/g) were purchased from Sigma-Aldrich. Glycerol (>99%), urea (>99%), GC (>99%), and methanol (>99%) were also obtained from Sigma-Aldrich. All materials were used without further purification.

2.2. Synthesis of polystyrene-supported metal containing imidazolium salt catalyst

The synthesis of PS-(Im)₂MX₂ was carried out *via* two steps (Scheme 1). First, bis[1-(2-hydroxyethyl)imidazolium]metal halide, (HEIm)₂MX₂, was synthesized by metal insertion [33,34] using an ethanol solution (100 mL) containing 1-(2-hydroxyethyl)imidazole (40 mmol) that was added to an ethanolic

solution (100 mL) of the metal halide (20 mmol). This mixture was stirred for 2 h at 50 °C and subsequently filtered. A crystalline solid was obtained after drying at 100 °C for 24 h under vacuum.

(HEIm)₂MX₂ was immobilized on polystyrene by alkoxylation as per our previous report [30,35]. A mixture of MPR (5 g), (HEIm)₂MX₂ (10 mmol), and acetonitrile (100 mL) was heated at 80 °C for 48 h in a 250-mL round-bottomed flask equipped with a condenser. After cooling the reaction mixture to room temperature, the solid was collected by filtration and washed several times with ethanol. The collected solid was dried at 80 °C for 24 h under vacuum. The supported catalysts were denoted PS-(Im)₂ZnI₂, PS-(Im)₂ZnBr₂, PS-(Im)₂ZnCl₂, PS-(Im)₂MgBr₂, and PS-(Im)₂CuBr₂, corresponding to the metal halides employed.

2.3. Characterization of PS-MIL catalyst

Elemental analysis (EA) of the samples was carried out using a Vario EL III instrument. The samples (2 mg) were heated to 1100 °C and sulfanilic acid was used as a standard. The Fourier transform infrared (FT-IR) spectra were acquired on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm⁻¹. The textural properties of the samples were analyzed by recording the N₂ adsorption isotherm at 77 K, using a BET apparatus (Microneritics ASAP 2020). Before gas sorption analysis, the samples were pretreated for 12 h at 120 °C under vacuum. The X-ray photoelectron spectroscopy (XPS) of the catalysts was conducted with the Theta Probe AR-XPS System X-ray source using monochromated Al K α radiation ($h\nu = 1486.6$ eV). Thermogravimetric analysis (TGA) was performed from room temperature to 500 °C on an AutoTGA 2950 apparatus under a nitrogen flow of 100 mL/min at a heating rate of 10 °C/min. The scanning electron microscopy (SEM) micrographs were acquired with a Hitachi S-47000 microscope operated at 30 kV. CO₂ and NH₃ temperature-programmed-desorption (TPD) profiles were acquired using a chemisorption analyzer (BEL-CAT) as follows: prior to measurements, 0.1 g of the sample was activated in He (30 mL/min) at 280 °C for 1 h. The sample was subsequently exposed to the pulses of CO₂ (10%) or NH₃ (10%) in He at 40 °C for 1 h. The sample was then flushed with He (30 mL/min) for 1 h. TPD measurements were carried out by raising the temperature from 40 to 300 °C at a heating rate of 5 °C/min.

2.4. Synthesis of glycerol carbonate from glycerol and urea

The synthesis of GC *via* the reaction of glycerol with urea was carried out in a 50-mL glass reactor equipped with a magnetic stirrer and condenser (Scheme 2). In a typical reaction run, the catalyst, glycerol, and urea were charged into the reactor. When the desired temperature was attained, the reaction was initiated by stirring under vacuum to remove ammonia as a by-product. The

Download English Version:

<https://daneshyari.com/en/article/39957>

Download Persian Version:

<https://daneshyari.com/article/39957>

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