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Significant influence of microwave dielectric heating on ionic liquid catalyzed transesterification of ethylene carbonate with methanol

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ABSTRACT

This paper reports an energy efficient route for the transesterification of ethylene carbonate (EC) with methanol using ionic liquid (IL) as catalyst through microwave heating. The influence of the reaction parameters such as the microwave irradiation time, power, EC/methanol ratio, and the cation and anion of both 1-alkyl-3-methyl imidazolium and tetraalkyl ammonium salts, was examined under these conditions. Also the heating characteristics of this reaction mixture were examined at various intervals. The coproduction of an equimolar amount of dimethyl carbonate (DMC) and ethylene glycol (EG) were obtained in high yield and better selectivity. Comparative studies were carried out under different reaction conditions with classical heating modes. An induction period observed during conventional reaction can be avoided by microwave dielectric heating. Overall, this study highlights an environmentally benign technology for the production of DMC, a "green reagent", through microwave irradiation.

1. Introduction

Microwave induced chemical reactions have become a popular technique for promoting faster organic synthesis to heat reaction mixtures, which is evidenced by the increasing number of publications and reviews [1–7]. This rapid and direct heating methods can reduce the reaction times from hours to minutes with high yield and purity of the product [8–11]. Ionic liquid (IL) represent a unique class of reaction media in catalytic processes, and their application in catalysis has entered a period of exploding growth. The use of room temperature IL as environmentally benign media for catalytic processes or chemical extraction is widely recognized and accepted on account of its unique properties, such as negligible vapor pressure, excellent thermal stability, tunable polarity, high coordinating ability, etc. [12–14]. Room temperature IL catalyzed chemical reactions provide excellent results with higher selectivity for the required product. Due to their ionic structure, ILs heat to high temperatures upon microwave irradiation. ILs are also ideal for use in microwave-promoted synthesis chemistry on account of their negligible vapor pressure and high thermal stability [15–17].

Dimethyl carbonate (DMC) a unique chemical compound with versatile reactivity that has found a diversified application in the chemical industry [18–20]. Due to its very high oxygen content, good blending octane values, freedom from phase separation, low toxicity and rapid biodegradability DMC has established its use as a possible gasoline-blending component. This "green reagent" has attracted considerable attention as a nontoxic substitute for dimethyl sulfate and phosgene which are both toxic and corrosive methylating and carbonylating agents [21,22]. In addition, it has the properties of solvents, reagents and the components needed for specialty materials. DMC is generally synthesized by a reaction between methanol and phosgene [23]. Considerable research has been carried out to establish an eco-friendly route for DMC production. A number of non-phosgene processes for preparing DMC have been developed but few of them are used commercially. In the mid-1980s, Enichem Synthesis patented a procedure for the production of DMC by the cuprous chloride catalyzed oxidative carbonylation of methanol in a slurry reaction system [24,25]. Recently, Ube Industry developed a novel DMC synthesis process that involves a Pd catalyzed reaction between methyl nitrile and carbon monoxide [26]. The above two processes used methanol, carbon monoxide and oxygen as raw materials. In contrast, the utilization of carbon dioxide as a raw material has been attempted, and some catalysts have been reported to be effective for the synthesis of DMC from methanol and carbon dioxide or from epoxide, carbon dioxide and methanol [27–33]. DMC can also be synthesized by a transesterification reaction between ethylene or propylene carbonate and methanol along with ethylene or propylene glycol. For this ester exchange reaction various catalysts, both homogeneous and heterogeneous have been reported to be efficient [34–38].

In this study, we monitored the microwave heating characteristics of EC–methanol reaction mixture in the presence of various ILs.

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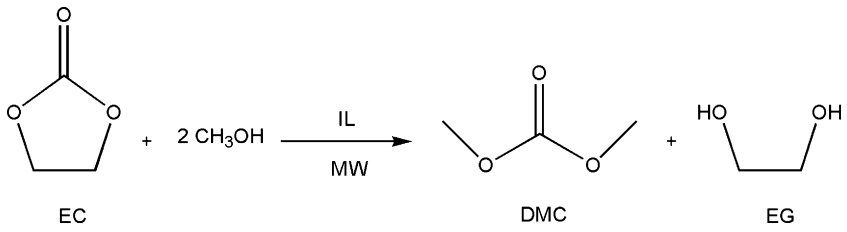

Scheme 1. Transesterification of ethylene carbonate with methanol.

Through this flash heating technique the transesterification for the coproduction of DMC and EG was established in a relatively short reaction time with high selectivity (Scheme 1) under mild reaction conditions. In our previous studies, different types of ILs were utilized as catalyst for transesterification reaction of EC or Propylene carbonate with methanol using conventional heating methods but high pressure of CO_2 is needed to stabilize EC from decomposition under these conditions [39,40].

2. Experimental

2.1. Materials

Anhydrous ethylene carbonate (99%) and anhydrous methanol (99.8%) were purchased from Aldrich and used without further purification. All types of ILs were kept in glove box under argon atmosphere and used without further purification. 1-*n*-butyl-3-methyl imidazolium chloride (BMImCl, ≥90.0%), 1-*n*-hexyl-3-methyl imidazolium chloride (HMImCl, ≥97.0%), 1-*n*-octyl-3-methyl imidazolium chloride (OMImCl, ≥97.0%), 1-ethyl-3-methyl imidazolium nitrate ($EMImNO_3$, ≥99.0%), 1-ethyl-3-methyl imidazolium trifluoro methane sulfonate (EMImOTf, ≥98%), tetrabutyl ammonium chloride (TBAC, ≥97%), tetraoctyl ammonium chloride (TOAC, ≥97%), tetradodecyl ammonium chloride (TDAC, ≥99%) and tetrabutyl ammonium bromide (TBAB, ≥99%) were purchased from Fluka chemicals. 1-Ethyl-3-methyl imidazolium chloride (EMImCl, 98%), tetrapropyl ammonium chloride (TPAC, 98%), tetrahexyl ammonium chloride (THAC, 96%), and tetrabutyl ammonium iodide (TBAI, 98%) were obtained from Aldrich. 1-Ethyl-3-methyl imidazolium hexafluoro phosphate ($EMImPF_6$, EP) was supplied by TCI laboratory chemicals.

2.2. Microwave equipment

Microwave irradiation was carried out in a multimode microwave reactor (Korea Microwave Instrument Corporation, KMIC 2000) with a continuously adjustable power from 0 to 2 kW using a 3-stub tuner operating at a frequency of 2.45 GHz. The surface temperature of the reactor was measured using an IR temperature detector. The reaction mixture was stirred with magnetic stirrer fixed under the microwave cavity.

2.3. Microwave induced transesterification of EC with methanol

All reactions were carried out in a 100 ml Pyrex glass reactor. A typical procedure is as follows: EC (2.2 g, 25 mmol), and the required amount of methanol (50–200 mmol) and IL (2 mmol) were placed in a reactor and capped inside the microwave cavity. The required microwave power was set and irradiated for the set time. The pressure inside the reactor was monitored using a pressure gauge, and for safety purpose a cracking pressure valve was set to 21 bar. After irradiation, the reactor was allowed to cool to room temperature and the products were analyzed by gas chromatography (Agilent6890, HP-5 column; 30 m, 0.320 mm, 0.25 μm, 60 to 325/350 °C) through comparison with authentic samples. EC conversion and DMC yield were obtained from the GC results. The products were identified by GC–MS (Agilent6890 GC (DB-5 column) fitted with a TOF-MS Pegasus III mass spectrometer). The yield of each product was calculated as the number of mol of the product formed per mol of the ethylene carbonate. For comparison, the reactions were carried out using a conventional process in a 50 ml stainless steel autoclave.

3. Results and discussion

In order to take the advantage of the microwave heating effect, it is preferable to carry out the reaction in the presence of a compound with high dielectric properties. Equimolar amounts of DMC and EG were produced in relatively good yield with high selectivity from the transesterification of EC with methanol in the presence of various ILs as catalysts. The temperature profile for the representative reaction mixtures as a function of irradiation time was probed and its significance on reaction is discussed in detail. Optimization of reaction condition was carried out by varying the reaction parameters such as the microwave irradiation time, microwave power, EC/methanol ratio and various types of ILs. For comparison, a series of conventional reactions were implemented at various reaction conditions. The detailed experimental results are reported in the following discussions.

3.1. Effect of reaction time and microwave power

The effect of the microwave irradiation time was studied using BMImCl as catalyst at 100 W microwave power. The results are shown in Fig. 1. It was demonstrated from the figure that EC conversion increased steadily with increasing reaction time until 30 min, subsequently the conversion of EC showed slight improvement. On the other hand, although the DMC yield increased in accordance with the EC conversion, the yield curve showed a plateau

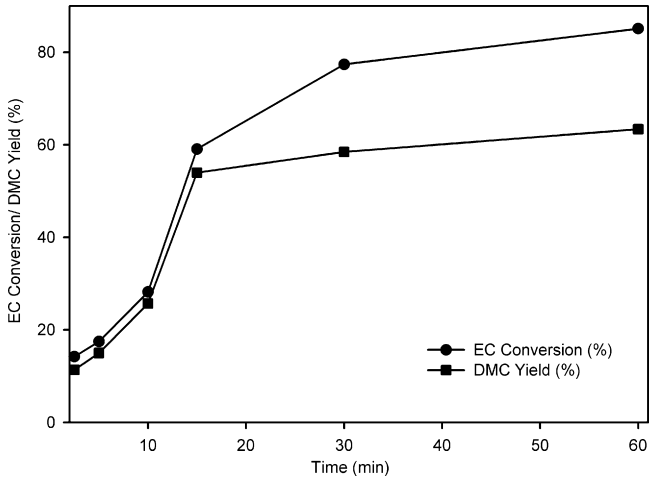

Fig. 1. Effect of reaction time (reaction conditions: EC/methanol/IL = 12.5/100/1, IL = BMImCl, MW power = 100 W).