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ScienceDirect

Procedia Engineering 148 (2016) 215 – 222

Procedia Engineering

www.elsevier.com/locate/procedia

4th International Conference on Process Engineering and Advanced Materials

Thermal stability and kinetic study of benzimidazolium based ionic liquid

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Abstract

3-methyl-1-(4-sulfo-butyl)-benzimidazolium trifluoromethanesulfonate [BSMBIM][CF_3SO_3] as a new ionic liquid (IL) was synthesized and their structure was confirmed by NMR, FTIR and CHNS technique. The IL thermal stability is of the great significance for their applications. This IL thermal stability was investigated by TGA from 373.15-873.15 K with different heating rates (10, 15 and 20°C). The activation energy and pre-exponential factor were also evaluated using Kissinger (171.01 KJ/mol and 9.88×10^{12} min^{-1}), Ozawa (172.60 KJ/mol and 13.76×10^{12} min^{-1}) and Starink (171.30 KJ/mol and 10.50×10^{12} min^{-1}) methods, respectively.

Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords:Ionic liquid; Thermal stability; Kinetics; Activation energy

1. Introduction

Ionic liquids (ILs) are the organic materials which are mostly in the liquid form below 100 ºC and solely composed of cations and anions [1, 2]. Ionic liquids benign substitutes for volatile organic solvents, especially in the area of green chemistry and have been described as potential environmentally in a variety of applications. Their unique

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Peer-review under responsibility of the organizing committee of ICPEAM 2016
doi:10.1016/j.proeng.2016.06.577

properties include high thermal stability, low volatility, and remarkable recyclability. ILs present admirable vast liquid range, dissolving capacity, and for both inorganic and organic materials as suitable solvents, etc. [2–5]. ILs composed by a combination of flexible cations/anions and has capable use in designs for specific tasks [6].

The thermogravimetric analysis (TGA) technique is commonly used for the kinetic study of devolatilization processes [3]. There are too many works described in the literature on the investigation and behavior of various materials using TGA such as water evaporation [4], rubber derivative [5], natural fibers [6], plastic [7] and different varieties of biomass [8, 9] during thermal degradation. The IL was synthesized and their onset temperature shows high-temperature range because some ILs are reported in the literature [10] and claim that they have high onset temperature and the present IL range is very near to that. It is reported that the decomposition temperature strongly depends upon the structure of IL [11]. Literature also reported that ILs decomposition temperature depends upon the cation type because imidazolium-based showed better thermal stability compared to pyridinium and ammonium based ILs [11-13].

Most of the ILs thermal decomposition, as well as kinetics, are still unknown. It might be due to a large number of available ILs and look impossible to measure the kinetics of all synthesized ILs. But it is a desire to determine the thermal decomposition of ILs on the basis of their structure [11]. Hao et al cited [14] the [Bmim]Cl and [Hmim]Cl ILs decomposition kinetics and reported the ILs short and long isothermal stability by few attempts. The mechanism of kinetics and thermal decomposition is quite important for the application.

The purpose of this work, to study the thermal stability and kinetic of the [BSMBIM][CF_3SO_3] by different reported methods. There is limited literature available on such type of study, but for specific high-temperature applications, a suitable selection and thermal decomposition of IL is important.

2. Experimental

All the chemicals (1,4-sultone, methylbenzimidazole, diethyl ether, trifluoromethanesulfonic acid) were obtained from Sigma-Aldrich (Malaysia), Merck (Germany) and used as received.

2.1. Synthesis of IL

1, 4-butanesultone was dissolved in toluene solvent contained in round bottom flask followed by adding a stoichiometric amount of 1-methylbenzimidazole under continuous stirring at room temperature for 72 hr. The resultant white solid (zwitterion) precipitate was filtered washed with diethyl ether and then dried under vacuum at 100°C for 5 hr. The dried white solid (zwitterion) was re-dissolved in distilled water and added the trifluoromethanesulfonic acid dropwise at room temperature and stirred it. After 30 minutes, the reaction was stirred for 6 hr at 60°C. The final deep yellow viscous ILs were subjected for washing with diethyl ether and then dried in vacuum. The synthesized IL is shown in Figure 1.

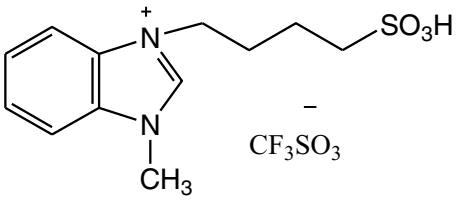

Fig. 1. Synthesised IL chemical structure.

2.2. Characterization

The structure was confirmed by NMR (Bruker Avance 500 MHz spectrometer), FTIR (Perkin Elmer-FTIR, spectrum one 54841), and elemental analysis (CE Instruments EA-1110). Coulometric Karl Fischer titration (Mettler