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A benign preparation of sec-butanol via transesterification from sec-butyl acetate using the acidic Imidazolium ionic liquids as catalysts

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HIGHLIGHTS

- Green synthesis of sec-butanol with an environmentally friendly catalyst was proposed.
- Screening of transesterification catalyst was performed.
- In the batch reactor, synthesis of sec-butanol was optimized using [HSO_3-PMIM]HSO_4 as catalyst.
- In the batch reactive distillation column, the conversion of sec-butyl acetate reached 97.72% under the optimized conditions.
- The acidic ionic liquids ([HSO_3-PMIM]HSO_4) showed high catalytic activity and reuse performance on the transesterification.

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ABSTRACT

Five acidic Imidazolium ionic liquids (ILs) were synthesized and the catalytic activity for the preparation of sec-butanol via the transesterification of sec-butyl acetate (SBAC) with methanol were investigated. Among them, 1-(3-sulfopropyl)-3-methylimidazolium hydrogen sulfate ([HSO_3-PMIM]HSO_4) performed best. In the batch reactor, the influences of various reaction conditions on the transesterification were investigated using [HSO_3-PMIM]HSO_4 as catalyst. Under the optimal reaction conditions, the conversion of SBAC was 89.30%. In addition, in order to enhance the conversion of SBAC, reactive distillation was carried out in the presence of [HSO_3-PMIM]HSO_4 as catalyst. A high conversion of the SBAC of 97.72% was obtained under the optimal reaction conditions. In order to evaluate the catalyst stability, the ILs was repeatedly used for 5 times without obvious loss of activity after simple separation from the mixture. The results indicated that [HSO_3-PMIM]HSO_4 showed better catalytic activity and reuse performance. Therefore, an environmental friendly technology for the preparation of sec-butanol catalyzed by ILs is provided.

1. Introduction

Sec-butanol is an important chemical material, which is widely used as emulsifiers, plasticizers, mineral-dressing agent, dye dispersants, etc. Also, it is used for the co-solvents of methanol in order to improve the octane number of gasoline. In addition, sec-butanol is one of the most essential chemical intermediates, which are widely used in the preparation of various chemicals. And the production of methyl ethyl ketone (2-butanone, MEK) is its main application, especially, accounting for about 90% of its total consumption [1,2]. In recent years, the increasing demands for MEK in the industry are more and more attractive, while the technology of the production of MEK lies in the preparation of the sec-butanol. Traditionally, sec-butanol has been produced through the hydration process of n-butene with water in the presence of sulfuric acid as catalyst [3]. However, this process is gradually phased out because of some serious and unavoidable disadvantages such as equipment corrosion, and excessive equipment investment. Afterwards, for the hydration process, many homogeneous and heterogeneous catalysts have been successfully developed, such as heteropolyacid, resin, and molecular sieve [3–5]. Although significant progress has been made, there remain many disadvantages, such as requiring high reaction temperature and reaction pressure, more consumption of energy, high purity for the n-butene, short life of catalyst and suffering from low conversion per pass of n-butene (<10%), more difficulties in separation and purification of the product from the reaction mixture.

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Therefore, the development of an efficient, stable, environmentally friendly catalyst and green process for the preparation of sec-butanol is very important. Sec-butyl acetate (SBAC) has high octane number, non-toxic, non-corrosion, and low oxygen content, which can replace methyl tert-butyl ether (MTBE) as the gasoline additive. So it has got wide application in industry [6]. However, with the change of the state regulations (SBAC was prohibited from adding in the gasoline), it is urgent to develop downstream products. Therefore, the preparation of sec-butanol via transesterification [7], hydrogenation [8] and hydrolysis [9] process utilizing SBAC as raw material is very attractive.

ILs is a new type of catalysts and solvents, in recent years, which has attracted much attention from the scientific and industry community as relatively clean and promising media because of their specially attributes, such as negligible vapor pressure, non-volatile, wide liquid range, high catalytic activity and thermal stability, easy recoverability and designability [10–13]. Those properties overcome the disadvantages of both traditional molecular solvents and melt salts. Indeed, ILs with Lewis and Brønsted acid site, have been found performed well in numerous applications involving esterification [14–16], dehydration [17–19], hydrolysis [20–22], polymerization [23,24], Friedel–Crafts acylation [25], etc. Nevertheless, until recently, their direct use as catalyst for the preparation of sec-butanol via transesterification reactions has rarely been reported in the literature.

In this paper, the synthesis and characterization of the five Brønsted acidic Imidazolium ILs and their use for the transesterification of SBAC with methanol for sec-butanol production in the batch reactor and reaction distillation column had been studied. The acidity, stability and reuse performance of those ILs were also investigated.

2. Experimental section

2.1. Materials

SBAC was obtained from Zhejiang Realsun Chemical Industry Co., Ltd. with a purity of >99.5%. Other chemicals (AR grade) were commercial products and used without further purification.

2.2. Preparation and characterization of acidic Imidazolium ILs

2.2.1. Preparation of acidic Imidazolium ILs

In this study, five acidic Imidazolium ILs were synthesized according to the procedures previously reported in the literature [26–29], Which included [BMIM]HSO$_4$, [HSO$_3$-BMIM]HSO$_4$, [HSO$_3$-PMIM]HSO$_4$, [HSO$_3$-PMIM]p-TSA, [HSO$_3$-PMIM]CH$_3$SO$_3$. The structures of the ILs were illustrated in Fig. 1.

2.2.2. Characterization of acidic Imidazolium ILs

NMR spectra were obtained on a Bruker AV500 spectrometer in DMSO-d6 and calibrated with TMS as the internal reference. IR measurements of ILs were recorded using a Spectrum 2000 FT-IR absorption spectrometer for KBr pellets in the frequency range from of 4000–400 cm^{-1}. The acidity of ILs was determined by using the theoretical model and UV–visible spectroscopic methods. UV–visible spectra were performed on Elmer Lambda 900 spectrometer with a basic indicator (4-nitroanline) by following the literature reported previously [30,31], and the solvent was methanol.

2.3. Experimental apparatus and procedure for sec-butanol synthesis

The batch experiment of the transesterification was carried out in a 500 ml cylindrical stainless steel reactor with mechanical stirring, sampling outlet, and temperature-controlling device (±0.1 °C) (Fig. 2). SBAC, methanol and ILs catalyst with specific ratio were introduced into the reactor. The transesterification was allowed to proceed at a certain temperature and pressure under stirring with a constant speed. The samples were withdrawn from the reactor at regular intervals, and cooled to room temperature. Afterwards, the qualitative analysis of all chemicals of the sample can be determined according to the retention time point of the gas chromatographic of its pure substance, and the samples were quantitatively analyzed by gas chromatography (GC) to determine the content of component.

The batch reactive distillation experiment of the transesterification was performed in a three-neck flask (0.5L) with a column (internal diameter of 22 mm and height of 1 m). The column was equipped with an electronic reflux splitter to control reflux ratio. The experimental setup of batch reactive distillation was shown in Fig. 3. The column was packed with the θ stainless steel packing ($\varphi 3 \times 3$). To minimize the heat losses to the surroundings, the column walls are covered with a rock wool insulating sheet. Reactants and catalyst with specific ratio were introduced into the bottom. First, total reflux operation was lasted for 1 h. Then the reflux ratio was increased to 1 (for 2 h), and finally increased to 3. The experiment should not be stopped until the temperature of the top of tower surpasses 57.0 °C (The methyl acetate mass concentration of the bottom was below 1%). After the completion of the reaction, samples were collected from the distillate and bottom, and analyzed quantitatively on GC. The ILs from the reaction mixture could be easily separated from mixture of the bottom by removing the unreacted materials and products with the Rotary Evaporator (80 °C, 15 mm Hg), and reused for the next time.

2.4. Sample analysis method

Quantitative analysis of sample with internal method was performed on a gas chromatography (GC 2014, Shimadzu

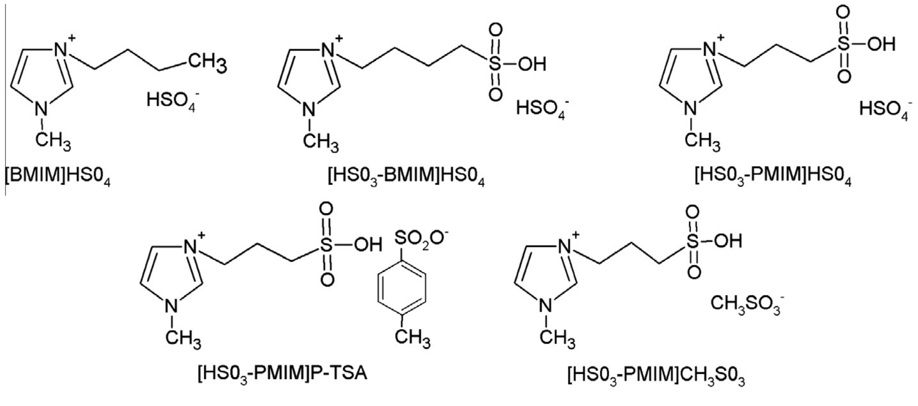

Fig. 1. Structures of the five acidic Imidazolium ILs.