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Kinetics of phenol alkylation with *tert*-butyl alcohol using sulfonic acid functional ionic liquid catalysts

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ABSTRACT

N-methyl imidazole, pyridine and triethylamine based Bronsted acidic ionic liquids with sulfonic acid ($–SO_3H$) functionality were obtained using 1,4-butane sultone. They were tested in a batch reactor for catalytic activity in the *tert*-butylation of phenol with *tert*-butyl alcohol (TBA). The reaction time, reaction temperature and reactant mole ratio were optimized. Among the three ionic liquids, triethylammonium based sulfonic acid functionalized ionic liquid was found to be the most promising and gave the highest phenol conversion. A maximum phenol conversion of 86% with 57.6% selectivity to 4-*tert*-butylphenol (4-TBP) was achieved at a temperature of 70 °C at a low ionic liquid to phenol ratio. The catalyst retained its activity even after 5 recycles. A kinetic model was developed for the reaction mechanism based on the product distribution and the kinetic parameters were estimated. The activation energy for ionic liquid catalyzed alkylation of phenol was found to be 11.13 kcal/mol in the temperature range of 50–90 °C. Negative activation energy was observed for 2-*tert*-butylphenol (2-TBP) to 2,4-di-*tert*-butylphenol (2,4-DTBP) and the extended Arrhenius equation was used to interpret this trend.

1. Introduction

Alkylation of phenol with *tert*-butyl alcohol yields butylated phenols which find use as raw materials in the production of antioxidants, phenolic resins, agrochemicals, rubber chemicals, printing ink, varnish, surface coatings, fungicides, ultraviolet absorbers, petroleum additives and heat stabilizers for polymeric materials [1–9]. Both homogenous and heterogeneous catalysts have been reported in the *tert*-butylation of phenol which include Lewis acid, $AlCl_3$ and BF_3 [10], Bronsted acids such as H_3PO_3, H_2SO_4, HF and $HClO_3$ [11], cation exchanged resins [7], zeolites [2,7], mesoporous materials [3,9], heteropoly acids [9], super critical and near critical water [5]. The major drawbacks of liquid acid catalysts include their hazardous, corrosive nature and tedious work-up involved in the separation of these catalysts from the reaction mixture. The solid acid catalysts have the problem of rapid deactivation due to coke formation due to pore blocking and also spent catalyst disposal problems. The cation-exchanged resins show good performance but are thermally unstable and fouling of resin is still a major issue.

In recent years, room-temperature ionic liquids (RTILs) have growing potential applications as environmentally benign alternative reaction media for both solvent and organic transformations [12–14]. The advantages of ionic liquids are negligible vapor pressure, thermal stability and good recoverability and recyclability [15,16]. The literature includes very few reports in the use of ionic liquids as catalysts in the alkylation of phenol with *tert*-butyl alcohol. Recently, Shen et al. reported high phenol conversion and 2,4-DTBP selectivity in the *tert*-butylation of phenol using Lewis acidic functionalized ionic liquid [bmim]PF_6 [7,8]. The major disadvantage of using Lewis acidic ionic liquids is the decomposition of IL forming hydrofluoric acid. Gui et al. compared various task specific imidazolium salts [6]. By tethering an alkane sulfonic group to the cation, they prepared Bronsted acid functionalized ionic liquids and achieved higher phenol conversion and selectivity to 2,4-DTBP in the *tert*-butylation of phenol. However, the drawback of imidazolium salts is that they are toxic due to the presence of imidazolium cation [17]. Henceforth, there is a need to develop environmentally benign catalysts which facilitate high phenol conversion and desired product selectivity along with easy recoverability and recyclability. Also, detailed kinetic investigations on promising ionic liquid catalysts are still scarce in the literature. Hence, the present work reports the preparation and characterization of sulfonic acid Bronsted acidic functionalized ionic liquids using low cost chemicals of triethylamine, pyridine and 1-methyl imidazole. These three different compounds were chosen, on the basis of literature reports [12–16] on compounds which can give lower viscosity ionic liquids, to study the effect of the anion in this alkylation reaction. The relative acidity of these

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functionalized ionic liquids measured by Hammett function, confirms that their acidity is almost equal to sulfuric acid [18]. Detailed kinetic investigations of phenol alkylation with TBA using the best of the prepared catalysts are also reported here.

2. Experimental

2.1. Materials and reagents

All the experiments were conducted using commercially available solvent and chemicals, used without further purification. N-methylimidazole, pyridine, triethylamine and 1,4-butane sultone were purchased from Sigma–Aldrich Chemicals Pvt. Ltd., India. Phenol and *tert*-butyl alcohol were purchased from Merck & CDH, New Delhi, India.

2.2. Preparation of ionic liquids

Sulfonic acid functionalized Bronsted acidic ionic liquids were prepared in the laboratory adopting the literature procedure [19,20]. N-methylimidazole was mixed with 1,4-butane sultone by stirring at 40–80 °C for about 24 h. After solidification, the zwitterion mass was washed three times using ethyl ether and dried under vacuum. Stoichiometric amount of sulfuric acid is added to the zwitterions and the mixture was stirred at 80 °C for 8 h to obtain the ionic liquid. Similar, procedure was adopted in the preparation of triethylamine and pyridine ionic liquids. The structures of the ionic liquids are presented in Fig. 1.

The prepared ionic liquids were characterized using NMR techniques and the results are as follows:

IL-1 (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate): ^{1}H NMR (D_2O, 400 MHz): δ (ppm) 1.16 (t, 9H, J = 6.8 Hz), 1.65 (m, 4H), 2.58 (t, 2H, J = 7.1 Hz), 3.13 (t, 2H, J = 8.0 Hz), 3.19 (m, 6H, J = 6.9 Hz); ^{13}C NMR (D_2O, 100 MHz): δ (ppm) 8.00, 20.69, 22.76, 51.04, 23.87, 56.65.

IL-2 (1-(4-sulfonic acid) butyl pyridinium hydrogen sulfate): ^{1}H NMR (DMSO, 400 MHz): δ (ppm) 1.58 (t, 2H), 2.01 (t, 2H), 2.62 (t, 2H, J = 7.5 Hz), 4.63 (t, 2H, J = 7.3 Hz), 8.15 (t, 2H, J = 7.6 Hz), 8.60 (t, 1H, J = 7.4 Hz), 9.09 (d, 2H, J = 7.0 Hz): ^{13}C NMR (D2O, 100 MHz): δ (ppm) 22.16, 30.60, 51.16, 61.21, 128.99, 145.66, 146.41.

IL-3 (1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate): ^{1}H NMR (D_2O, 400 MHz): δ (ppm) 1.55 (t, 2H), 1.87 (t, 2H), 2.59 (t, 2H, J = 7.9 Hz), 3.84 (s, 3H), 4.17 (t, 2H, J = 6.9 Hz), 7.7089 (d,1H), 9.15 (d,1H), 10.30 (s,1H); ^{13}C NMR (D_2O, 100 MHz): δ (ppm) 22.28, 29.31, 36.58, 49.28, 51.24, 123.15, 124.48, 137.48.

2.3. Activity testing

The alkylation experiments were carried out in a sealed glass tube under autogeneous pressure. A typical batch contains 10 mmol each of phenol, *tert*-butyl alcohol and ionic liquid stirred at 800 rpm for 8 h. At the end of the reaction, the mixture was cooled and the products were extracted by toluene. A qualitative product analysis was conducted using GC–MS and quantitative analyses were conducted by separating the product mixture in a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column and flame ionization detector in a NUCON GC supplied by M/s AIMIL India Ltd.

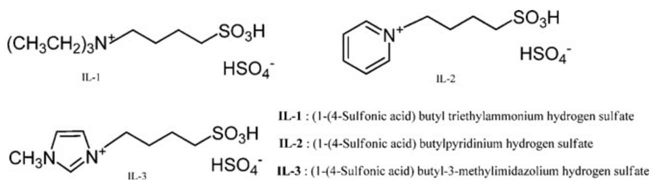

Fig. 1. Structure of ionic liquids.

3. Results and discussion

3.1. Comparison of activity of the three ionic liquids

The three ionic liquids were found to be thermally stable well above the reaction temperatures. Thermal decomposition temperatures of IL-1, IL-2 and IL-3 were observed to be 325.4 °C, 324.8 °C and 366.9 °C respectively when tested in a TA instruments TGA model SDT Q600 at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

The activity of the prepared ionic liquid catalysts in this reaction was compared with solid and liquid acid catalysts reported in literature, as shown in Table 1. From the table, it can be observed that the product distribution using the ionic liquid catalysts ranges from *ortho* and *para tert*-butyl phenol (2-TBP and 4-TBP) to dialkylated products 2,4-DTBP and 2,6-DTBP. No *meta*-TBP or ethers are observed even when the phenol conversion is high. Also, no oligomers were observed in the product. It is evident that all the three ionic liquids gave high phenol conversion and good selectivity to the desired products, 2-TBP and 2,4-DTBP at 70 °C compared to other catalysts. Although the [bmim] PF_6 ionic liquid shows a marginally higher conversion, yet, it has the disadvantage of forming HF during reaction. Ionic liquid catalyst, [hmim] 1,4-$(CH_2)_4SO_3$]HSO_4 also shows good conversion of phenol at 70 °C and 2:1 TBA to phenol ratio, but comparatively lower than the conversion obtained using IL-1 even at higher catalyst to phenol mole ratio (1.5:1). When similar catalyst to phenol mole ratio (1:1) was used, the conversion using [hmim] 1,4-$(CH_2)_4SO_3$]HSO_4 is lower compared to that obtained using all the three prepared ILs. Among the three ionic liquids, IL-1 (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate) gave the maximum conversion and good selectivity to 2,4-DTBP (2,4-di-*tert*-butylphenol) at the given temperature. Hence, detailed kinetic investigations were conducted using IL-1 catalyst, which is also the cheapest of the prepared catalysts [17].

3.2. Effect of reaction time on phenol conversion

Fig. 2 shows the effect of reaction time on conversion of phenol at 70 °C using 1:1 molar ratio of phenol to TBA and 1:1 molar ratio of phenol to IL-1 (N-(4-sulfonic acid) butyl triethylammonium

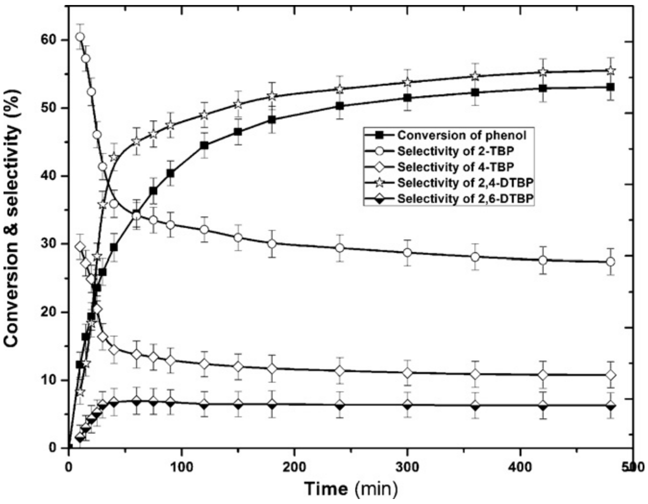

Fig. 2. Effect of reaction time on phenol conversion and product selectivity. Reaction conditions: phenol (10 mmol):TBA:IL-1 (1:1:1) mole ratio at 70 °C.