Applied Catalysis A: General 506 (2015) 228–236

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Highly efficient alkylation of phenol with *tert*-butyl alcohol using environmentally benign Bronsted acidic ionic liquids

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ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 22 August 2015
Accepted 25 August 2015
Available online 28 August 2015

Keywords:
Ionic liquids
Alkylation
Phenol
tert-Butyl alcohol
tert-Butylation
2,4-Di-*tert*-butylphenol
Density functional theory

ABSTRACT

A series of SO_3-H functionalized environmentally benign Bronsted acidic ionic liquids were prepared using triethylamine, 1-methyl imidazole, pyridine, diethanolamine, 1,4-butane sultone and methane sulfonic acid as the starting materials. These synthesized ionic liquid catalysts were characterized using spectroscopic tools like ^{1}H NMR, ^{13}C NMR. The catalytic activity of the synthesized ionic liquids was investigated in *tert*-butylation of phenol with *tert*-butyl alcohol. The effect of kinetic parameters like reaction time, reaction temperature, reactant mole ratio, reactant to catalyst mole ratio, on the conversion of phenol and selectivity to 2-*tert*-butyl-phenol and 2,4-di-*tert*-butyl-phenol were investigated. Phenol conversion upto 94.2% was achieved at temperature as low as 80 °C and low alcohol to phenol molar ratio of 2:1, ionic liquid to phenol ratio of 1:1 and reaction time of 2 h. The catalyst was found to retain its activity even after 8 recycles and was completely recoverable. The plausible reaction mechanism was formulated based on product distribution. The kinetic data was found to agree well with classical phenomenological models and the kinetic parameters were estimated. The experimental results were further validated by Density Functional Theory (DFT) optimizations of the ionic liquid structures performed at the B3LYP/6-311G** level using Gaussian 09 package.

1. Introduction

Alkylation of phenol with *tert*-butyl alcohol (TBA) is an industrially important Friedel–Crafts reaction for the production of the fine chemicals, mainly 2-*tert*-butyl-phenol (2-TBP) and 2, 4-di-*tert*-butyl-phenol (2,4-DTBP) [1]. All the products of this reaction are important lipophilic phenols used in the production of antioxidants in food industry. These *tert*-butylated phenols are also used as additives in jet fuels, petroleum products, cosmetics, pharmaceuticals, rubber manufacturing, varnishes, printing inks and also as polymerization inhibitors, UV absorbers, antiseptic and embalming fluids [1–12]. Several investigations on the *tert*-butylation of phenol using both homogeneous and heterogeneous catalysts, Lewis acids like $AlCl_3$ and BF_3 [2], Bronsted acids like HF, H_3PO_4, H_2SO_4, and $HClO_3$ [3], mesoporous materials [4,5], near critical as well as super critical water [6], cation-exchange resins [7], zeolites [7,8], heteropoly acids [5], solid sulfanilic acids [9] are reported till date. However, most of the homogeneous liquid acid catalysts are environmentally hazardous due to their corrosive nature. The solid acids have the disadvantages of rapid deactivation by coking and pore blocking as well as solid waste disposal problem. The cation-exchange resins are not thermally stable to be used in industry [10]. Hence, the need for greener routes using environmentally benign catalysts is recognized by many researchers. During the last two decades, ionic liquids, with their tremendous potential both as solvents and catalysts have evolved immensely as a solution to most of the problems involving catalytic reactions. Room temperature ionic liquid (RTIL) catalysts, with negligible vapor pressure, ease of separation from reaction products, excellent thermal stability and almost complete recyclability, have been considered to be a solution for most of the above mentioned problems [11–20]. However, reports on alkylation of phenol with TBA using ionic liquid catalysts are scanty [13–20]. Moreover, Density Functional Theory (DFT) studies on correlating the properties of ionic liquids in catalytic reactions are almost negligible. Shen et al. reported imidazole based Lewis acidic ionic liquid, [bmim] PF_6 in catalyzing the alkylation of phenol with TBA [13,14]. However, these Lewis acidic ionic liquids produce corrosive acids. Gui et al. reported a set of imidazole based Bronsted acidic ionic liquids with SO_3-H as the active functional group. This process is, however, not viable for large scale alkylated phenols production because of the inherent toxicity of these ionic liquids due to the presence of the imidazole ring [18]. Elavarasan et al. reported a set of SO_3-H functionalized Bronsted acidic ionic liquids with 86% phenol conversion [20] and Liao et al.

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http://dx.doi.org/10.1016/j.apcata.2015.08.031

made an effort to correlate the activities of the Bronsted acidic ionic liquids using DFT optimizations of the structures in Gaussian 09 [21]. In the present study, we report highly energy efficient 94.2% conversion of phenol using environmentally benign SO_3-H functionalized room temperature ionic liquids in alkylation of phenol with TBA. DFT calculations were used to correlate the experimental acidity trends of these ionic liquids and hence, to explain their high catalytic activity in this reaction. Further those results were used to validate the effect of acidity and functionality variation on the alkylation mechanism.

The effect of kinetic parameters like reaction time, temperature, reactant mole ratio, catalyst to reactant mole ratio on phenol conversion were investigated and these parameters were optimized in a batch reactor. Based on the product distribution, a reaction mechanism was proposed for the alkylation of phenols using functionalized ionic liquid catalysts. The kinetic data was fitted to various models reported in literature [20] and the best fit model was used to estimate the kinetic parameters. The activation energy was finally calculated using the Arrhenius equation.

2. Experimental

2.1. Chemicals

A series of Bronsted acidic ionic liquids with SO_3-H functionality were synthesized following the procedure outlined in literature [20,22–24]. 1-Methyl imidazole was purchased from Sigma–Aldrich Chemicals Pvt., Ltd., UK. Triethylamine, pyridine and diethanolamine were purchased from Spectrochem Chemicals, India. 1,4-butane sultone wasw purchased from Sigma–Aldrich Chemicals Pvt., Ltd., Germany. Phenol and TBA ere purchased from Merck Chemicals Pvt., Ltd., Mumbai, India.

2.2. Synthesis of ionic liquids

As a general methodology for ionic liquid preparation, the individual amine was mixed with 1,4-butane-sultone and stirred at 60–80 °C for 12–18 h. Resultant zwitterionic solid was washed three times with diethyl ether and then dried under vacuum (120 °C, 0.01 Torr). Finally, equivalent amount of methane sulfonic acid was added to the solidified zwitterionic mass and stirred at 80 °C for 4–7 h to obtain the ionic liquid. The structures of the synthesized ionic liquids are shown in Fig. 1. All the chemicals were research grade and were used without further purification unless otherwise stated.

2.3. Characterization of synthesized ionic liquids

The prepared ILs were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy using Bruker ARX-300 spectrometer. Thermo gravimetric analysis (TGA) was performed using a TG 209 F3 Tarsus instrument. UV–vis spectra were recorded on a Shimadzu UV-2450 instrument.

2.3.1. Characterization of ionic liquids by NMR

IL-1 [N-(4-sulfonic acid) butyl triethylammonium methane sulfonate]: ^{1}H NMR (D_2O, 300 MHz): ∂ (ppm) 0.953 (t, 9H), 1.501 (m, 4H), 2.475 (s, 3H), 2.644 (t, 2H), 2.888 (t, 2H), 2.967 (q, 6H), ∂ (ppm) = 4.80 [Solvent peak (D_2O)]; ^{13}C NMR (D_2O, 75 MHz): δ(ppm) 4.301, 17.552, 18.975, 36.151, 47.677, 50.244, 53.600.

IL-2 [1-(4-sulfonic acid) butylimidazolium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 1.542 (m, 2H), 1.879 (m, 2H), 2.125 (s, 1H), 2.416 (s, 3H), 3.856 (s, 3H), 4.186 (t, 2H), 4.293 (t, 2H), 7.713 (d, 1H), 7.778 (d, 1H), 9.148 (s, 1H), δ (ppm) = 2.508 [Solvent peak (DMSO)]; ^{13}C NMR (DMSO, 75 MHz): δ (ppm) 21.065, 28.065, 30.274, 35.318, 48.044, 49.982, 121.895, 123.206, 136.209, δ (ppm) = 39.006 [Solvent peak (DMSO)].

IL-3 [1-(4-sulfonic acid) butylpyridinium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 1.615 (m, 2H), 2.022 (m, 2H), 2.281 (s, 1H), 2.580 (s, 3H), 2.603 (t, 2H), 4.677 (t, 2H), 8.169 (t, 2H), 8.613 (t, 1H), 9.096 (d, 2H), δ (ppm) = 2.511 [Solvent peak (DMSO)]; ^{13}C NMR (DMSO, 75 MHz): δ (ppm) 20.5389, 28.9577, 49.6571, 60.7467, 75.6754, 127.9776, 143.8474, 145.3695, δ (ppm) = 38.2471 [Solvent peak (DMSO)].

IL-4 [*N*,*N*-bis(2-hydroxyethyl)-(4-sulfonic acid)-1-aminium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): ∂ (ppm) 1.640 (m, 2H), 1.733 (m, 2H), 2.410 (s, 3H), 3.020 (m, 1H), 3.160 (m, 1H), 3.221 (t, 2H), 3.301 (t, 2H), 3.658 (t, 2H), 3.742 (t, 4H), 3.933 (broad m, 4H), ∂ (ppm) = 2.513 [Solvent peak (DMSO)]; ^{13}C NMR (DMSO, 75 MHz): δ (ppm) 21.790, 22.396, 49.280, 53.338, 55.913, 57.993, 63.651, δ (ppm) = 39.510 [Solvent peak (DMSO)].

2.3.2. Thermo gravimetric analysis of ionic liquids

The thermal decomposition temperatures of the ILs were obtained using TG 209 F3 Tarsus at a heating rate of 10 K/min, under nitrogen atmosphere. Thermal decomposition temperature of IL-1, IL-2, IL-3 and IL-4 were observed at 312 °C, 324.8 °C, 366.9 °C and 326 °C, respectively.

2.3.3. Acidity of ionic liquids

To compare the Bronsted acidity of different ionic liquids, UV–vis spectroscopy was used as mentioned in literature [25–30]. As a general methodology 4-nitro aniline (pK_a value of 0.99) was chosen as a basic indicator to abstract proton from the Bronsted acidic ionic liquids in water. The variation in acidity was evaluated in terms of the measurable ratio of the unprotonated and protonated indicator concentration ratio, $[B]_{aq}/[BH^+]_{aq}$. The Hammett function (H_0) was then calculated using Eq. (1) as shown below:

$$H_0 = \mathrm{p}K(B)_{\mathrm{aq}} + \log\left(\frac{[B_{\mathrm{aq}}]}{[\mathrm{BH}^+]_{\mathrm{aq}}}\right) \tag{1}$$

where, p$K(B)_{aq}$ is the pK_a value of the indicator in aqueous solution. The terms $[BH^+]_{aq}$ and $[B]_{aq}$ are protonated and unprotonated indicator molar concentrations in the solvents respectively. The blank solution of 4-nitro aniline in water showed absorbance maxima at 381 nm. Fig. 2a shows the absorbance of IL-1 solution at different concentrations. The Hammett function of the other ionic liquids prepared in the laboratory was also found by similar procedure, and the results are shown in the Fig. 2b. From the figure, it is clear that the four ionic liquids possess strong acidity which is very important for this acid-catalyzed reaction.

2.3.4. Catalytic testing

A series of activity tests using these laboratory synthesized ionic liquids were carried out in a 3 mL polytetrafluoroethylene (PTFE) sealed Borosil glass reactor under autogeneous pressure placed on a magnetic stirrer. In a typical batch run, 1 mmol each of phenol, TBA and ionic liquid were taken in the reactor and stirred for 5 h at 80 °C. The product mixture was analyzed both using a NUCON GC supplied by AIMIL India Ltd., equipped with a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column and flame ionization detector (FID). The carbon balance was checked and found to be more than 99.9% while ring balance was obtained to be more than 97.9%.

2.3.5. Computational methods

MATLAB 8.4 software version was used to perform the optimization in the kinetic modeling. The DFT studies were performed using Gaussian 09 software [31]. Geometry optimizations of different ionic liquids were performed at the B3LYP level using the 6-311++G (d, p) basis set. A vibrational analysis was also performed for each