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A Functionalized, Supported Ionic Liquid for Alkylation of *p*-Cresol with *Tert*-Butyl Alcohol

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Abstract

SO$_3$-H functionalized ionic liquid was prepared using 1-vinyl imidazole and 1,4 -butanesultone as source materials and then supported on mesoporous silica material (SBA-15). This supported ionic liquid catalyst was characterized using XRD, SEM, FT-IR, solid state NMR, TGA. Their catalytic activity in *Tert*-butylation of *p*-cresol with *tert*-butyl alcohol (TBA) was investigated in a batch autoclave. The effects of reaction time, reaction temperature, catalyst amount and reactant mole ratio on the conversion of *p*-cresol and 2-*tert*-butyl-*p*-cresol (TBC) and 2, 6-di-*tert*-butyl-*p*-cresol (DTBC) selectivities were investigated. Lower alcohol to *p*-cresol mole ratios, lower catalyst loading at 110°C gave a 65% maximum conversion of *p*-cresol. The recoverability and recyclability of the catalyst was also investigated. The catalyst could be completely recovered and its activity was found to be almost completely retained even after 5 recycles. The experimental data was found to satisfy a second order rate equation. The activation energy was calculated to be 5.2 kcal/mol.

Keywords: Supported ionic liquids; *p*-cresol; Butylated hydroxytoluene; *Tert*-butylation; Kinetics

Introduction

Friedel-Crafts alkylation of aromatic compounds with alkyl halides, alcohols, alkenes or ethers as alkylating reagents is an important reaction that has been used in the production of pharmaceuticals and fine chemicals for more than a century [1]. Alkylation of *p*-cresol with *tert*-butyl alcohol (TBA) gives 2-*tert*-butyl-*p*-cresol (TBC) and 2, 6-di-*tert*-butyl-*p*-cresol (DTBC) called butylated hydroxytoluene (BHT). These are used as antioxidants in food industry and in jet fuels, petroleum products, cosmetics, pharmaceuticals, rubber manufacture, and also as embalming fluids, antiseptics, polymerization inhibitors, UV absorbers [2-4]. Butylated hydroxytoluene (BHT), is an important lipophilic phenol mainly used as plastic, elastomer antioxidant and petroleum additive. Earlier catalysts used for the production of alkylated *p*-cresols include Lewis acids (AlCl$_3$, FeCl$_3$ and ZnCl$_2$) [5], Bronsted acids (H$_3$PO$_4$, H$_2$SO$_4$, HF, HClO$_4$) [6], cation exchange resins [7], mesoporous materials [8], nano-materials [9-11], zeolites [12], sulfated zirconia [13], heteropolyacids [14] and also supercritical and near-supercritical fluids [15]. All these catalysts have drawbacks which limit their use in a continuous process for BHT production. The liquid acid catalysts cause equipment corrosion and environmental pollution while solid acids deactivate rapidly. Although cation-exchange resins showed promise, thermal stability and fouling of the resins pose major problems for their commercialization [7]. Recently, there has been an increasing interest in developing catalytic processes with minimum environmental threats and maximum economic benefits.

Room temperature ionic liquids which came to light with their growing applications as alternative reaction media for organic transformations and separations have also be used as acid catalysts [16-19]. They possess important attributes, such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability and ease of separation of products from reactants. Alkylation of *p*-cresol with TBA in acidic ionic liquids has been reported to give good product selectively and high yield of 2-TBC [20,21]. However, this is a homogeneous reaction at room temperature and has a disadvantage of consuming large amounts of organic solvent for the ionic liquid recovery and recycling. To avoid this problem, it is important to heterogenize the ionic liquids by immobilizing on a catalytically active or neutral solid supports and develop novel heterogeneous catalysts. Sugimura et al. immobilized acidic ionic liquids by copolymerization with styrene as catalysts for acetalization [22] and Qiao et al. prepared ionic liquid catalyst supported over silica gel and used it in esterification and nitration reactions [23].

In this paper, we aim at heterogenizing a laboratory synthesized ionic liquid catalyst on SBA-15, and activity testing in the alkylation reaction of *p*-cresol with TBA, so that the process can be easily scaled-up for industrial production of BHT. This report details an efficient and environmentally benign alkylation reaction of *p*-cresol with TBA using SO$_3$-H functionalized ionic liquid supported on SBA-15 which has considerable surface silanol groups compared to SiO$_2$ and MCM [24]. Another advantage of choosing SBA-15 as the support is that it has a hexagonal array of uniform tubular channels with high pore diameter larger than MCM-41 and has lower diffusional resistance. Also, SBA-15 has higher thermal and hydrothermal stability because of higher wall thickness compared to MCM-41. This supported ionic liquid was characterized using various techniques described below and the catalytic activity including the effects of kinetic parameters like reaction time, temperature, reactant ratio, amount of catalyst and catalyst recyclability were investigated in a batch reactor.

Experimental

p-Cresol, *tert*-butyl alcohol, vinylimidazole, 1,4-butane sultone, Tetraethyl orthosilicate (TEOS) and mercapto propyl triethoxy silane (MPTES) were purchased from Sigma Aldrich Chemicals Pvt. Ltd, India. All chemicals were of analytical reagent (A.R.) grade. These were used as received without any further purification.

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Catalyst preparation

Preparation of Bronsted acidic ionic liquid: In a typical ionic liquid preparation procedure [22,23], 0.1 mol of 1-allyimidazole was taken and equal amount of 1, 4-butane sultone was added slowly under liquid nitrogen (Scheme 1). The mixture was then stirred at room temperature for about 24 h until it turned into solid zwitterions. After solidification, the zwitterions mass was washed three times with ethyl ether and dried under vacuum (25°C, 0.01 Torr). Stoichiometric amount of sulfuric acid was then added to the precursor zwitterions slowly under liquid nitrogen. The mixer was stirred at 60°C for 12 h. The liquid product was washed with diethyl ether and dried in vacuum at 50°C.

Thiol functional mesoporous silica materials: A typical procedure for synthesis of thiol functional SBA-15 is as follows [25,26]: 4 g of Pluronic 123 was dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated to 40°C before addition of TEOS. A TEOS pre-hydrolysis time of 45 min was used prior to the addition of the thiol precursor [MPTMS] to the mixture. The molar composition of the mixture for 4 g of copolymer was 0.0369 TEOS: 0.0041 MPTMS: 0.24 HCl: 6.67 H_2O. The resultant solution was stirred for 20 h at 40°C, after which time the mixture was transferred into a Teflon-lined stainless steel autoclave at 100°C for 24 h under static conditions. The solid product was recovered by filtration and dried at 60°C in air overnight. The template was removed from the as-synthesized material by washing with ethanol under reflux for 24 h (1.5 g of as-synthesized material per 400 mL of ethanol).

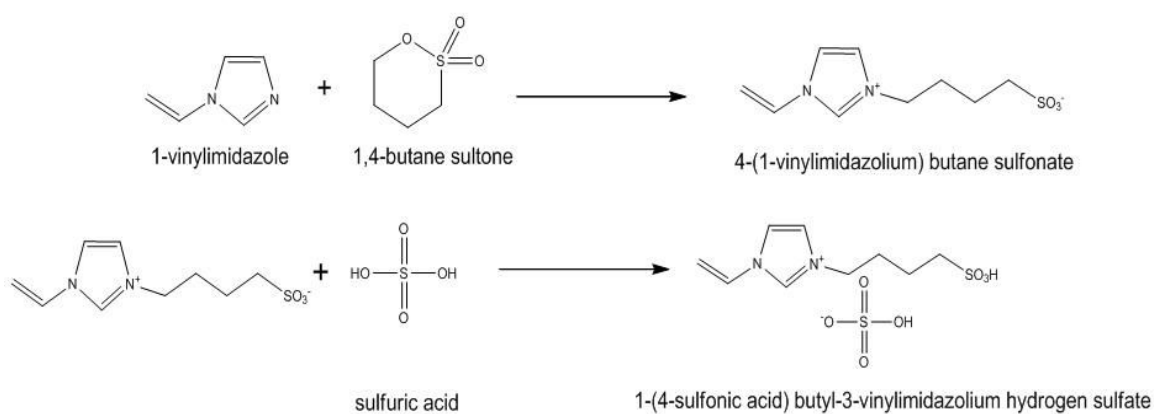Preparation of supported ionic liquids: 2 g of thiol functional SBA-15, 10 mmol acidic ionic liquid, 100 ml acetonitrile and 5mol% azodiisobutyronitrile (AIBN) were added to ionic liquid successively [23]. The reaction was then carried out under reflux for 30 h. The precipitate was filtered and washed with solvents like acetonitrile followed by acetone and then diethyl ether. It was then dried in vacuum at 80°C for 5 h. (Scheme 2).
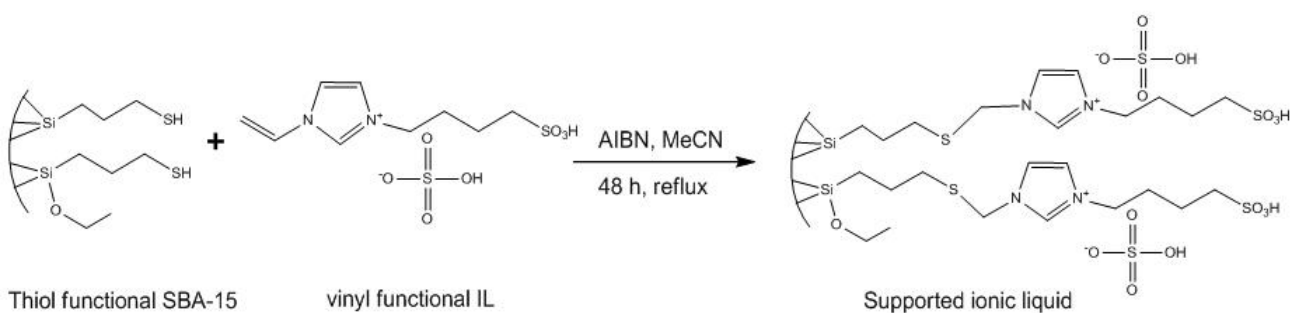
Catalyst characterization

The supported ionic liquids were characterized by ^{13}C NMR spectroscopy using Bruker ARX-400 spectrometer. X-Ray powder diffraction (XRD) data were acquired on a Philips X'pert pro PW3040 diffractometer using Cu-Kα radiation. The data were collected from 0.5 to 4º (2θ) with a low resolution. The thermal stability data for the solids was obtained by NETZSCH Thermo Microbalance TG 209 F3 Tarsus at a heating rate of 10°C/min under nitrogen. The surface morphology was characterized using SEM (Zeiss EVO 50) and the transmission spectra recorded on a Nicolet-6700 FTIR instrument were used to check the presence of the thiol functional groups after SBA-15 surface modification.

Activity testing

The supported ionic liquids were tested for their activity in this reaction in a 30 ml stainless steel autoclave lined with a Teflon bomb and equipped with a magnetic stirrer. A typical batch consisted of 10 mmol each of *p*-cresol, TBA and 250 mg of supported ionic liquid reacted under autogeneous pressure. Reaction temperature was maintained at 70°C and reaction mixture was stirred for 3 hours. A qualitative product analysis was conducted in a GC-MS and quantitative analyses were conducted in a NUCON GC model 5765 supplied from M/s

Scheme 1: 1-Allyimidazolium contained SO_3H functional ionic liquids.

Scheme 2: Supported ionic liquid.

AIMIL India Ltd. using a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column for product separation and a flame ionization detector.

Results and Discussion

Characterization results

Figure 1 shows the XRD patterns of SBA-15 (a), functionalized SBA-15 (b) and supported ionic liquid (c) respectively. These exhibit well resolved peaks corresponding to the 100, 110, and 200 planes of the 2-D hexagonal mesostructured [27]. As is evident from (b) and (c), the smaller XRD peaks decreased in intensity considerably after functionalizing the SBA-15. Due to the addition of organosilanes which have both organic and inorganic moieties even after hydrolysis and disturb the formation and self-assembly of the SBA-15 mesostructured.

The powder morphologies of SBA-15, thiol functionalized SBA-15 and IL supported SBA-15 are shown in Figure 2. The SEM images reveal that the IL supported SBA-15 have cylindrical uniform size and length. These images indicate that the structure of SBA-15, modified SBA-15 are stable, IL loaded SBA-15 are uniform under the magnification used except for a little dispersion in the IL loaded SBA-15, similar observation was reported by Wang et al. for phenyl functionalized SBA-15 [28].

Figures 3 shows the FTIR transmission spectra of SBA-15 (a), functionalized SBA-15 (b) and IL supported SBA-15 (c). S-H vibration peak is clearly observed at 2560 cm^{-1} on spectrum (b), which indicated that MPS was successfully grafted on the surface of SBA. Both the peaks of S-H and the allyl group totally disappeared in the supported ionic liquid shown by spectrum (c) [29]. This shows that the ionic liquid was successfully grafted on the modified SBA-15 via the route shown in Scheme 2 [20]. Further evidence to this successful grafting is seen in Figure 4, the solid-state ^{13}C NMR spectrum of 4a, the high field shifted signal at 21.7 ppm belongs to the C-1 closest to the Si and 70.0 ppm, 80.4 ppm belong to C-2 and C-3 respectively, before the immobilization of IL [24]. Figure 4b spectrum which represents the immobilized ionic liquid on SBA-15, shows the peak shift to 56.6 ppm for C-4, C-8, C-11 and similarly, 26.5 ppm, 33.5 ppm can be assigned to C-10, C-9 respectively. C-5, C-6 and C-7 represent the aromatic carbons and their assigned chemical shifts are 127.4 ppm, 135.4 ppm and 140.4 ppm.

The thermal analysis was carried out in the temperature range from 40 to 800°C, in air at a heating rate of 10°C/min. The TGA pattern of SBA-15 demonstrates that there are two observable weight loss regions as shown in Figure 5. The region for all the three samples lies between ambient to 100°C and this is attributed to the loss of physically bound water and breakup of hydrogen bonded network [24]. In the Figure 5(a), weight loss was observed for thiol functionalized SBA-15 between 150°C to 400°C which is due to the desorption of the adsorbed water as well as water generated by the condensation of a part of free silanols. In the Figure 5(b), weight loss was observed for thiol functionalized SBA-15 at 315°C (approximately 30%) which is due to the loss of thiol group on the surface of the solid. In the Figure 5(c), weight loss of the supported ionic liquid is observed at three places: one at 215°C (approximately 10%), which is corresponding to the decomposition of the residual copolymer, second at 300°C (approximately 20-25%), which is due to the loss of ionic liquid on the surface of solid. and the last region at 350°C and beyond (approximately 20%) is due to the loss of deposited coke on the surface of the solid. The TGA of the supported ionic liquid show that it is stable in the range of the reaction temperature (70°C to 120°C).
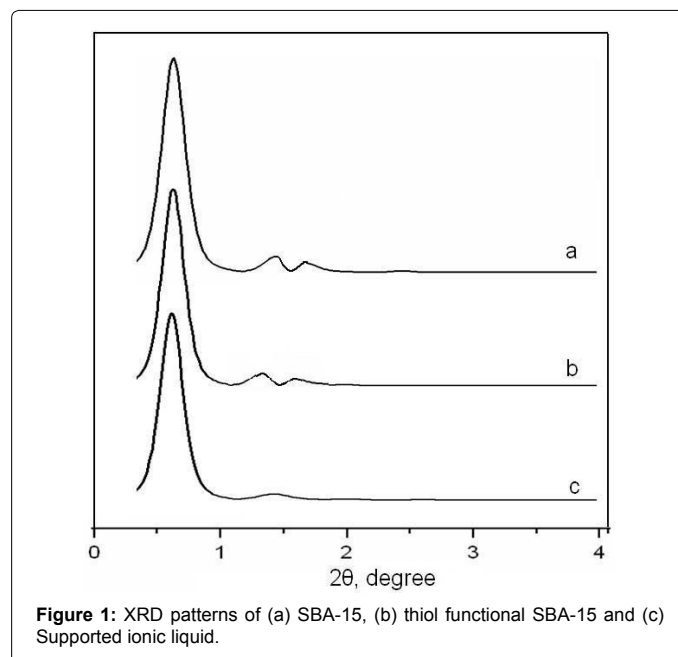

Figure 1: XRD patterns of (a) SBA-15, (b) thiol functional SBA-15 and (c) Supported ionic liquid.
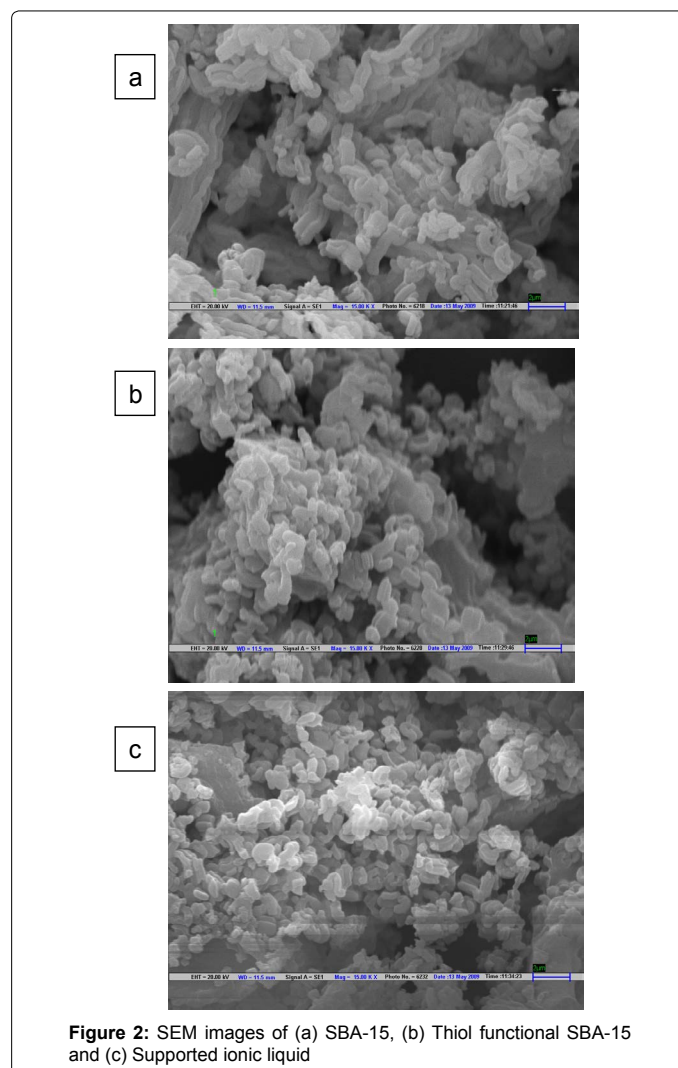

Figure 2: SEM images of (a) SBA-15, (b) Thiol functional SBA-15 and (c) Supported ionic liquid
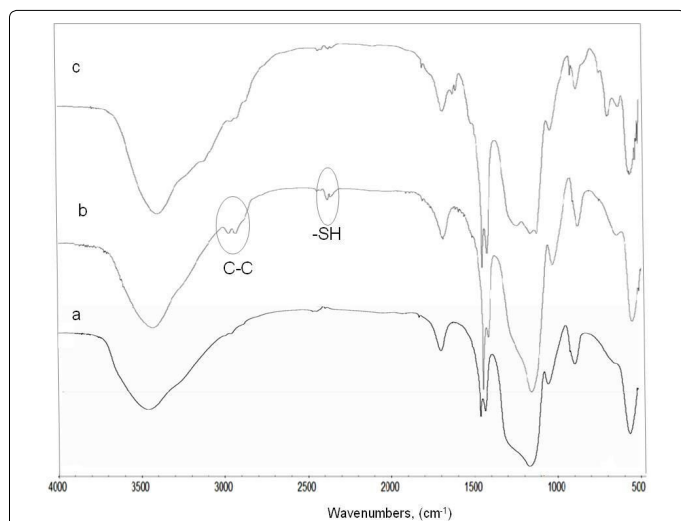
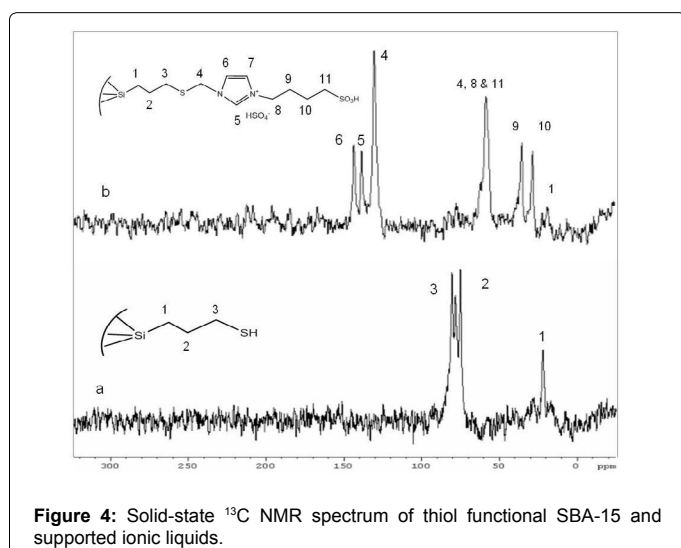**Figure 3:** FTIR spectrum of (a) SBA-15, thiol functional (b) SBA-15 and (c) Supported ionic liqiud.

Figure 4: Solid-state ^{13}C NMR spectrum of thiol functional SBA-15 and supported ionic liquids.
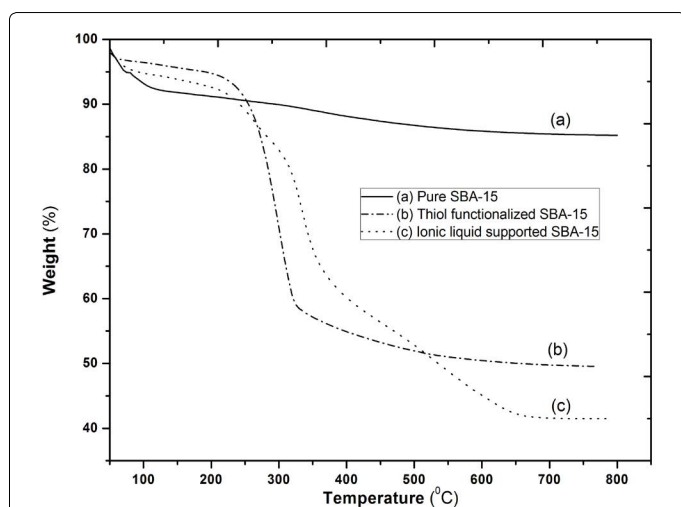

Figure 5: TGA analysis. SBA-15 (a), thiol functionalized SBA-15 (b), supported ionic liquid (c).

Effect of reaction time on p-cresol conversion

The influence of reaction time on conversion of *p*-cresol and selectivity to TBC and DTBC was investigated at different temperatures and different reactant mole ratios. Figure 6 shows the conversion of *p*-cresol at 90°C, 1:1 molar ratio of *p*-cresol to TBA and 25 wt% supported ionic liquid with respect to *p*-cresol during reaction time of 3 hours. The alkylation of *p*-cresol with TBA over this catalyst shows high selectively to TBC, 2,6-di-*tert*-butyl-3-methyl phenol (DTBC). Among the products, *p*-cresyl-*tert*-butyl ether (CTBE) was also observed. With increase in reaction time, the conversion of *p*-cresol and selective yield of TBC and DTBC increased and reached an equilibrium level after 2 hours and remained almost constant thereafter, the selective yield of ether decreased during this time. The conversion of *p*-cresol reached 65%, the selectivities to TBC and DTBC reached 72% and 12% respectively after 2 hours. The ether was formed initially and converted to TBC which explains its decreased selectivity with time.
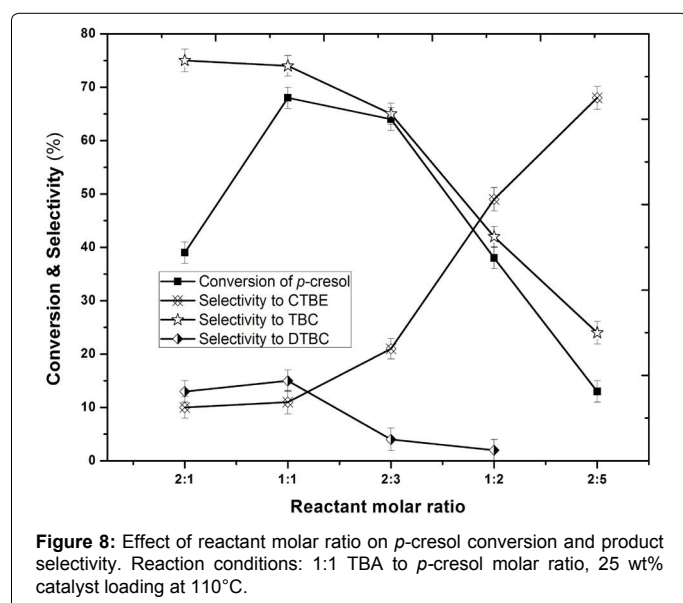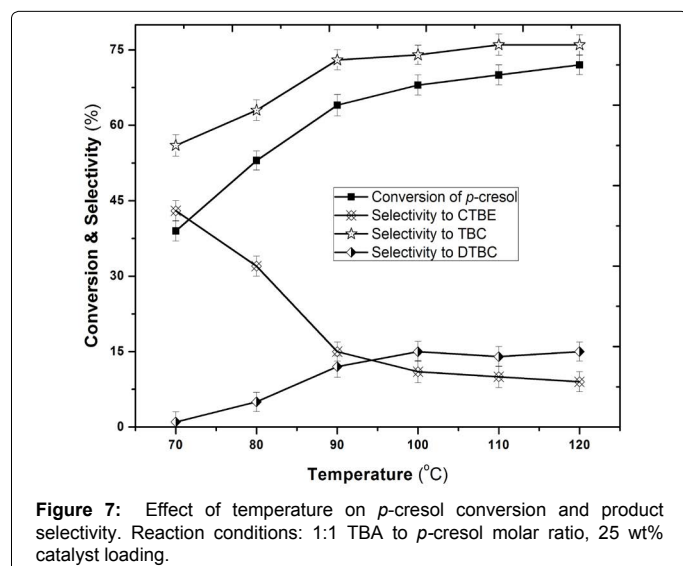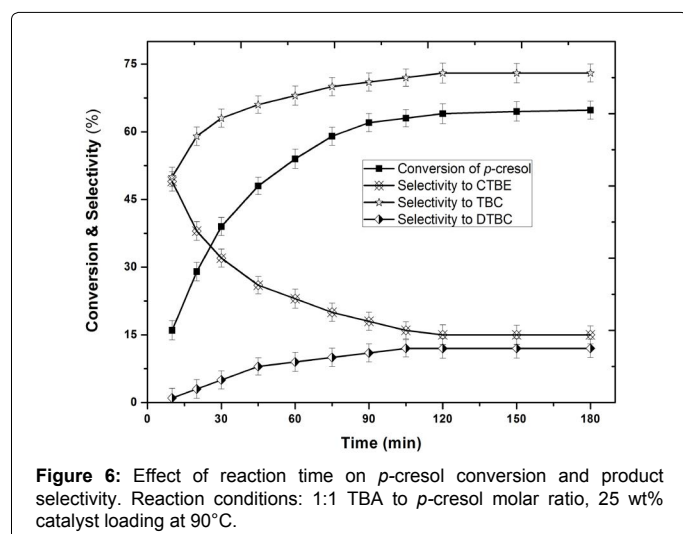
Effect of reaction temperature

The reaction was investigated in the temperature range of 70°C to 120°C. Figure 7 shows the variation of *p*-cresol conversion and the product selectivities with temperature. At 70°C, the conversion of *p*-cresol is 36% and increased to 72% at 120°C. The selectivity to ether is high (45%) at 70°C and as the temperature is increased, the selectivity to ether decreases. This decrease in selectivity to ether is due to the migration of O-alkylated product to C-alkylated product. The highest selectivity to TBC was found to be 76% at 110°C, TBA: *p*-cresol mole ratio of 1:1 and 250 mg of catalyst (25 wt% of IL). The TBC selectivity is due to its higher stability and the availability of solvated *tert*-butyl cation at this temperature. At temperatures 100°C and above oligomer products (10%) were observed due to the oligomerization of isobutene formed from dehydration of the alcohol similar to the observation made by our group when the ionic liquid was used as the catalyst [21]. Considering conversion and selectivities, the optimum reaction temperature is 110°C.

Effect of molar ratio of TBA to *p*-cresol

The effect of molar ratio on *p*-cresol conversion and product selectivity was studied at 110°C using 250 mg of supported ionic liquid catalyst with TBA to *p*-cresol molar ratio varying between 0.5 to 4 and the results are shown in Figure 8. For a constant catalyst loading, it was observed that as the amount of TBA increases, the conversion of *p*-cresol and yield of TBC passed through a maximum, while selectivity to TBC passed through a minimum. The maximum *p*-cresol conversion was observed when the molar ratio was 1. Conversion of *p*-cresol decreased when molar ratio of TBA and *p*-cresol was more than 1, this is because of the progressive dilution of the ionic liquid with water, which was formed during the dehydration of TBA. This affects the conversion of *p*-cresol as well as the formation of unwanted oligomerized and O-alkylated products. Hence, the optimum mole ratio of 1:1 *p*-cresol to TBA was used in further investigations.

Effect of amount of catalyst in the reaction system

The effect of catalyst loading on *p*-cresol conversion, TBC and DTBC selectivities was investigated using supported ionic liquid to *p*-cresol ratio from 0.5 to 3 at 110°C and TBA and *p*-cresol molar ratio constant at 1:1, which can be shown in Figure 9. As catalyst loading is increased, the *p*-cresol conversion and TBC selectivity increased to maximum at a catalyst loading of 25 wt% of reaction mixture and thereafter, decreased. This may be attributed the significant mass transfer resistances at higher catalyst loading. High conversion of

Figure 6: Effect of reaction time on *p*-cresol conversion and product selectivity. Reaction conditions: 1:1 TBA to *p*-cresol molar ratio, 25 wt% catalyst loading at 90°C.

Figure 7: Effect of temperature on *p*-cresol conversion and product selectivity. Reaction conditions: 1:1 TBA to *p*-cresol molar ratio, 25 wt% catalyst loading.

Figure 8: Effect of reactant molar ratio on *p*-cresol conversion and product selectivity. Reaction conditions: 1:1 TBA to *p*-cresol molar ratio, 25 wt% catalyst loading at 110°C.

p-cresol and high selectivity to TBC was achieved, when catalyst loading and *p*-cresol molar ratio was maintained at 1:1 at 110°C.

Recoverability and recyclability of ionic liquid

In order to examine the recoverability and recyclability of the supported ionic liquid, the supported ionic liquid was filtered after the reaction and washed with solvents in the order of toluene, acetone, diethyl ether and ethanol followed by centrifugation and dried under vacuum for 5 hr at 80°C. After vacuum drying, the catalyst was reused and the results of the catalytic recycling experiments are shown in the Table 1. The catalyst was completely recoverable and could be repeatedly used 5 times without major loss of *p*-cresol conversion and product selectivity.

Kinetic study

The kinetic runs were carried out at five different temperatures 353, 363, 373, 383 and 393 K respectively at autogeneous pressure. Figure 7 shows the conversion of *p*-cresol at various temperatures. Detailed reaction mechanism of *tert*-butylation of *p*-cresol using functional ionic liquid catalyst was studied elsewhere [21]. The system can be described by the reactions given in Scheme 3. The reaction occurs in the ionic liquid phase but not on surface of the solid. The kinetic investigations were carried out in the absence of any external and intra-particle mass transfer limitations. A second order rate model was found to fit the kinetic data well and is shown in Figures 8-10. The Arrhenius plot, Figure 11, was used to evaluate the activation energy and frequency factor for this temperature dependent kinetics. The values of the activation energy and frequency factor in the temperature range of 80 to 120°C are 5.2 kcal/mol and 2.32 respectively. The activation energy values compare well with the values for *p*-cresol alkylation reactions using ionic liquid, near-critical water, cation exchanged resins, sulfated zirconia reported in literature. Activation energy for alkylation of *p*-cresol with TBA using ionic liquid catalyst was 15.63 kcal/mol in the temperature range of 50-90°C [21]. Activation energy for alkylation of *p*-cresol in near critical water was 29 kcal/mol in the temperature range of 250-300°C [15]. Activation energy for this reaction over sulfated zirconia was reported as 22.88 kJ/mol in the temperature ranges of 30-120°C [13]. Activation energy of 23.2 Kcal/mol was reported over cation exchanged resins in the temperature ranges of 34-70°C [7]. As compared to the batch alkylation of *p*-cresol over other catalysts, the activation energy using supported ionic liquid catalyst is low showing that the reaction is controlled by intrinsic kinetics.

Conclusion

SO_3-H functionalized ionic liquid which was prepared in the laboratory was successfully supported on thiol functionalized SBA-15 and characterized. This supported ionic liquid was found to be catalytically active in *tert*-butylation of *p*-cresol with TBA when the

S No	Experimental Run	% Conversion of *p*-cresol	% Selectivity		
			CTBE	TBC	DTBC
1	Fresh	70	9	74	13
2	Recycle 1	71	10	75	13
3	Recycle 2	70	9	75	13
4	Recycle 3	71	10	74	12
5	Recycle 4	71	10	73	14
6	Recycle 5	69	9	75	13

Reaction conditions: *p*-cresol; TBA (1:1) molar ratio; 25 wt% catalyst loading at 110°C, 3 h.

Table 1: Recyclability of supported ionic liquid catalyst.

Scheme 3: *Tert*-butylation of *p*-cresol with *tert*-butyl alcohol over supported ionic.
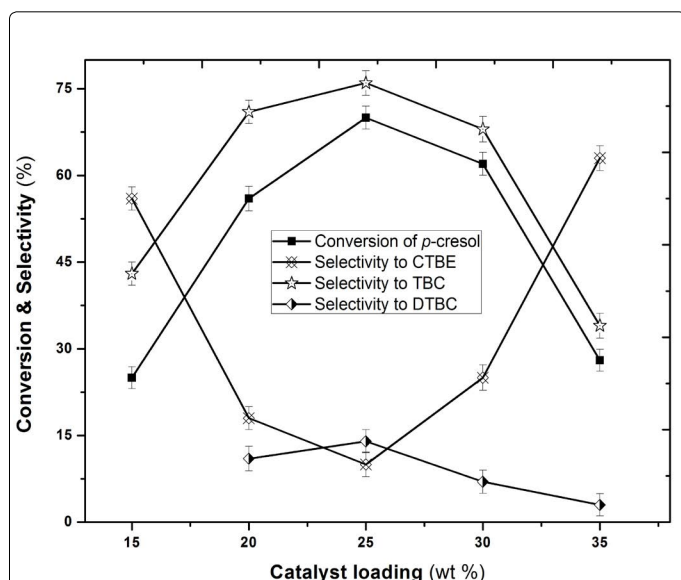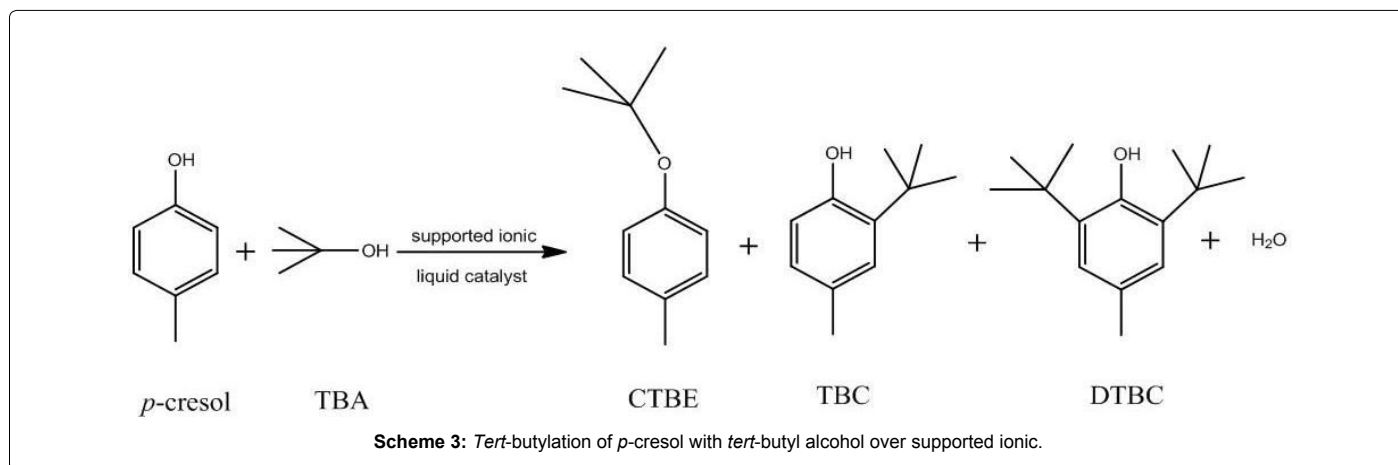

Figure 9: Effect of catalyst loading on *p*-cresol conversion and product selectivity. Reaction conditions: 1:1 TBA to *p*-cresol molar ratio at 110°C.
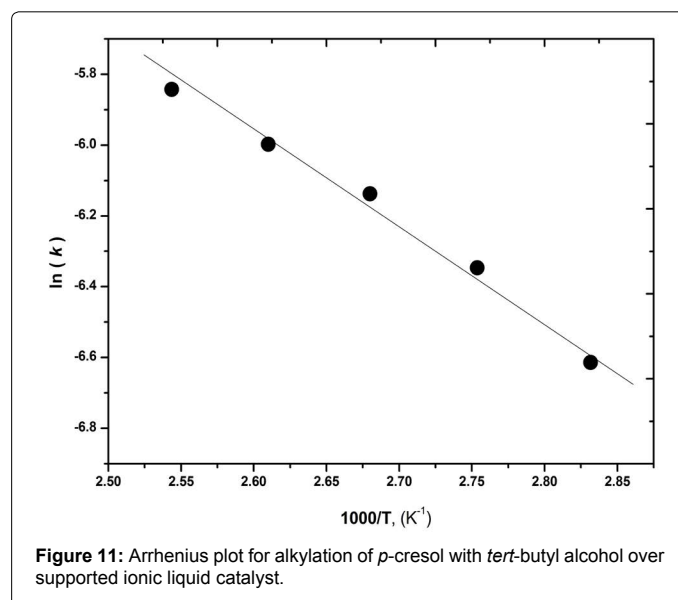

Figure 11: Arrhenius plot for alkylation of *p*-cresol with *tert*-butyl alcohol over supported ionic liquid catalyst.
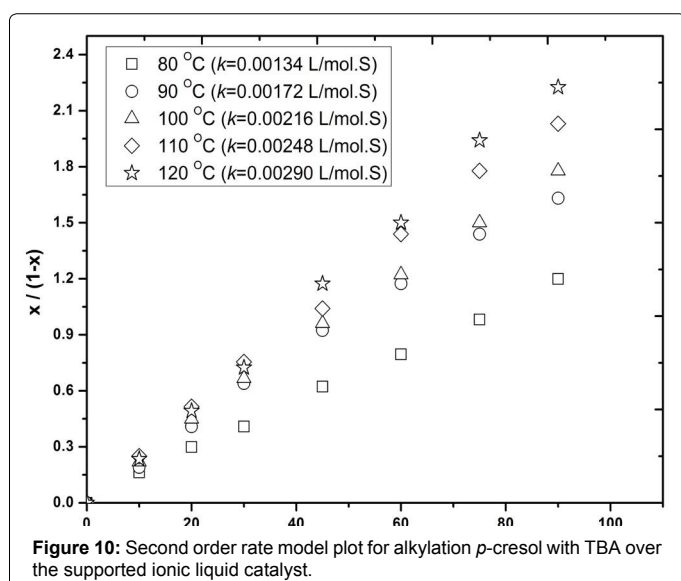

Figure 10: Second order rate model plot for alkylation *p*-cresol with TBA over the supported ionic liquid catalyst.

reaction was investigated in a batch autoclave under autogeneous pressure. Catalyst showed no leaching of the IL during reaction. The supported IL catalyst could be recovered completely and reused after removal of water under vacuum. A maximum of 65% *p*-cresol conversion and 76% TBC selectivity was obtained at the optimum conditions of 110°C, 1:1 reactant mole ratio and 25% catalyst loading in the reaction mixture. The activation energy for this reaction over this catalyst was found to be 5.2 kcal /mol in the temperature range of 80 to 120°C, which is lower than that obtained over other solid acid catalysts researched so far. Thus, these Bronsted acidic supported ionic liquid catalysts which do not require use of a solvent for recovery, show promise for the development of a continuous environmentally benign, energy efficient and economical process route for the production of TBC and BHT.

References

1. Olah GA (1963) Friedel-crafts and Related Reactions. Interscience, New York, USA.

2. Pilato LA, Knop A (1985) Phenolic Resins. Chemistry, Applications and Performance, Future Directions. 1st edn. Springer, Berlin.

3. Pospisil J (1988) Poly Deg Stab 20: 181-202.

4. Murphy J (2001) Additives for Plastics Handbook. 2nd edn. Elsevier, Amsterdam.

5. Kirk RE, Othmer DF, Kirk-Othmer G (1978) Concise Encyclopedia of Chemical Technology. 3rd edn. Wiley Interscience, New York, USA.

6. Sears CA Jr (1948) Alkylation of phenol with iota-butyl alcohol in the presence of perchloric acid. J Org Chem 13: 120-122.

7. Santacesaria E, Silvani R, Wilkinson P, Carra S (1988) Alkylation of p-cresol with isobutene catalyzed by cation-exchange resins: a kinetic study. Ind Eng Chem Res 27: 541-548.

8. Selvaraj M, Kawi S (2007) Micropor Mesopor Mater 98: 143-149.

9. Moradi O, Yari M, Zare K, Mirza B, Najafi F (2012) Carbon Nanotubes: Chemistry Principles and Reactions: Review. Fullerenes Nanotubes and Carbon Nanostructures 20: 138-151.

10. Ahmadpour M, Eftekhari N, Ayati A (2014) Performance of MWCNTs and a low-cost adsorbent for Chromium(VI) ion removal. J Nanostruct Chem 4: 171-178.

11. Zare K, Gupta VK, Moradi O, Makhlou ASH, Sillanpaa M, et al. (2015) A comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: a review. J Nanostruct Chem 5: 227-236.

12. Zhang K, Zhang H, Xu G, Xiang S, Xu D, et al. (2001) Appl Catal A 207: 183-190.

13. Yadav GD, Thorat TS (1996) Kinetics of Alkylation of p-Cresol with Isobutylene Catalyzed by Sulfated Zirconia. Ind Eng Chem Res 35: 721-731.

14. Usha Nandhini K, Herbert Mabel J, Arabindoo B, Palanichamy M, Murugesan V (2006) Micropor Mesopor Mater 96: 21-28.

15. Chandler K, Liotta CL, Eckert CA, Schiraldi D (1998) Tuning alkylation reactions with temperature in near-critical water. AIChE J 44: 2080-2087.

16. Welton T (1999) Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. Chem Rev 99: 2071-2084.

17. Chowdhury S, Mohan RS, Scott JL (2007) Tetrahedron 63: 2363-2389.

18. Wasserscheid P, Keim W (2000) Ionic Liquids-New "Solutions" for Transition Metal Catalysis. Angew Chem Int Ed Engl 39: 3772-3789.

19. Sheldon R (2001) Catalytic reactions in ionic liquids. Chem Commun (Camb). pp: 2399-2407.

20. Liu X, Zhou J, Guo X, Liu M, Ma X, et al. (2008) SO3H-Functionalized Ionic Liquids for Selective Alkylation of p-Cresol with tert-Butanol. Ind Eng Chem Res 47: 5298-5303.

21. Kondamudi K, Elavarasan P, Dyson PJ, Upadhyayula S (2010) Alkylation of p-cresol with tert-butyl alcohol using benign Bronsted acidic ionic liquid catalyst. J Mol Catal A 321: 34-41.

22. Sugimura R, Qiao K, Tomida D, Yokoyama C (2007) Immobilization of acidic ionic liquids by copolymerization with styrene and their catalytic use for acetal formation. Catal Commun 8: 770-772.

23. Qiao K, Hagiwara H, Yokoyama C (2006) Acidic ionic liquid modified silica gel as novel solid catalysts for esterification and nitration reactions. J Mol Catal A 246: 65-69.

24. Melero JA, Stucky GD, Grieken R, Morales G (2002) Direct syntheses of ordered SBA-15 mesoporous materials containing arenesulfonic acid groups. J Mater Chem 12: 1664-1670.

25. Li J, Qi T, Wang L, Liu C, Zhang Y (2007) Synthesis and characterization of imidazole-functionalized SBA-15 as an adsorbent of hexavalent chromium. Mater Lett 61: 3197-3200.

26. Shon JK, Yuan X, Ko CH, Lee HI, Thakur SS, et al. (2007) Design of Mesoporous Solid Acid Catalysts with Controlled Acid Strength. J Ind Eng Chem 13: 1201-1207.

27. Liu Y, Peng J, Zhai S, Li J, Mao J, et al. (2006) Synthesis of Ionic Liquid Functionalized SBA-15 Mesoporous Materials as Heterogeneous Catalyst toward Knoevenagel Condensation under Solvent-Free Conditions. European J Inorg Chem 2006: 2947-2949.

28. Wang XM, Du XZ, Li CL, Cao X (2008) Direct synthesis and characterization of phenyl-functionalized SBA-15. Appl Surf Sci 254: 3753-3757.

29. Rac B, Molnar A, Forgo P, Mohai M, Bertoti I (2006) A comparative study of solid sulfonic acid catalysts based on various ordered mesoporous silica materials. J Mol Catal A 244: 46-57.