Reusable and Efficient Polystryrene-supported Acidic Ionic Liquid Catalyst for Mononitration of Aromatic Compounds

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A series of polystyrene-supported 1-(propyl-3-sulfonate)-3-methyl-imidazolium hydrosulfate acidic ionic liquid (PS-[SO₃H-PMIM][HSO₄]) catalysts were prepared and tested for mononitration of simple aromatics compounds with nitric acid. It was found that the reactivity of the catalysts increased with increasing [SO₃H-PMIM][HSO₄] content. The para-selectivity was not only related to the [SO₃H-PMIM][HSO₄] content but also the substituent groups in aromatics. A reaction mechanism of nitration over this new catalyst was proposed. The catalytic activity of this catalyst decreased slightly after fifth runs in the synthesis of nitrotoluene.

Key Words : Polystyrene-supported acidic ionic liquid, Nitration reaction, Simple aromatics
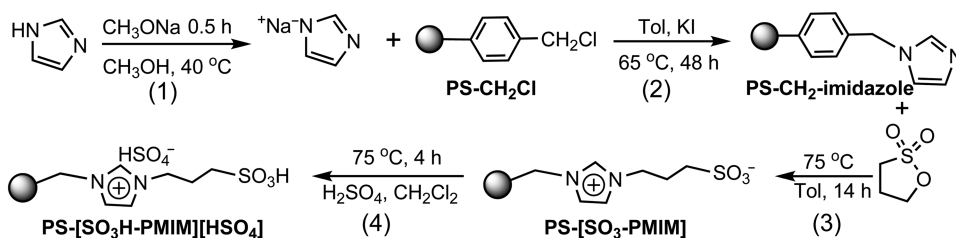
Introduction

Nitration of aromatic compounds is a fundamental reaction. Traditionally, they are performed with mixture of nitric and sulfuric acids, which is not environmental friendly and often provides poor selectivity. Various clean nitration approaches[1-3] have therefore been explored in order to avoid these insufficient. Since the end of last century, with more and more recognition of room temperature ionic liquids (TSILs), a growing interests have also been witnessed in ionic liquids as solvents or catalysts for aromatic nitration. Aromatics nitration in imidazole based ionic liquid,[4-7] *N*-(4-hydroxysulfonylbutyl) pyridinium based ionic liquid,[8] quaternary ammonium based ionic liquid[9] and tetra-alkylphosphonium ionic liquids[10] were reported in succession. Although much success has been achieved, some problems still remained, for example, needing of a lot of ionic liquid, inconveniences in a continuous system and even some separation problems when they were used in some homogeneous reaction systems such as nitration of aromatic compounds with aqueous nitric acid.

Later, some nitration reactions catalyzed by supported ionic liquids have been reported. Qiao[11] immobilized acidic ionic liquid to modified silica gel and used it to catalyze the nitration of aromatic compounds with 62% nitric acid. Recently, Wang[12] reported a new nitration system of PEG200-

based dicationic acidic ionic liquid/N₂O₅ for aromatic nitration. In our previous work, our group reported[13] halogen-free SO₃H-functional Brønsted-acidic ILs that could efficiently catalyze the nitration of aromatic compounds. As part of our continuing interest in this aspect, here, we supported a imidazole type Brønsted-acidic TSILs, 1-(propyl-3-sulfonate)-3-methy-imidazolium hydrosulfate acidic ionic liquid ([SO₃H-PMIM][HSO₄]), onto chloromethylated polystyrene beads to prepare a series of PS-[SO₃H-PMIM][HSO₄] catalyst, and tested for monoitration of aromatics compounds with nitric acid. The catalyst was characterized by FT-IR, SEM/TEM, elements analysis, TG/DSC and acid base titration. The effect of [SO₃H-PMIM][HSO₄] content on the nitration results were investigated carefully.

Experimental

Catalyst Preparation. Scheme 1 showed the synthetic process of PS-[SO₃H-PMIM][HSO₄].[14-16] First, sodium methylate (0.1 mol) in methanol (10 mL) was added dropwise into the mixture of imidazole (0.1 mol), KI (0.1 g) and toluene (5 mL) at 40 °C. Then, PS-CH₂Cl beads (0.01 mol, -CH₂Cl), prepared according document,[17] in acetonitrile (15 mL) was added to the formed imidazole sodium salt solution, the reaction was carried out at 65 °C for 48 h. The PS-CH₂-imidazole product was filtered off and washed by

Scheme 1. Synthesis of PS-[SO₃H-PMIM][HSO₄] catalyst.

soxhlet extraction using ethanol as solvent and dried under vacuum. Second, PS-CH$_2$-imidazole and equiv (relative to -imidazole) 1,3-propane sultone were added in anhydrous toluene and reacted at 75 °C for 14 h. Then PS-[SO$_3$-PMIM] product was filtered off, washed with toluene and dried under vacuum. Last, dried PS-[SO$_3$-PMIM] was soaked in dichloromethane at 0 °C, and acidified with equiv concentrated sulfuric acid. The mixture was heated to 75 °C for 4 h under stirring. The target catalyst PS-[SO$_3$H-PMIM][HSO$_4$] was filtered off, washed with diethyl ether and dried under vacuum.
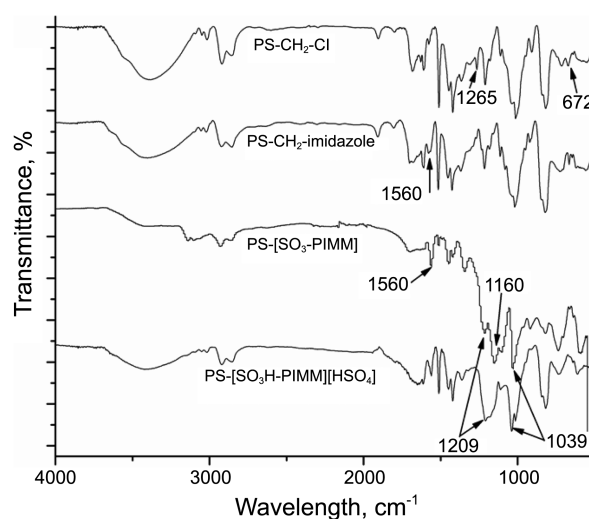
Catalyst Characterizations. IR spectra was recorded using a Nicolet IS10 FTIR spectrometer. TG/DSC studies were carried out using METTLER TOLEDO SDTA851e/DSC823e instrument. Elemental analysis was determined by Vario MICRO EL. SEM was recorded on a Leica S440i. GC spectra was recorded using a Agilent GC-6820 spectrometer. Acidic sites was confirmed by titration of PS-[SO$_3$H-PMIM][HSO$_4$] catalyst with 2.08×10^{-2} M aq. NaOH, using phenolphthalein as indicator.

Catalyst for Aromatics Mononitration Reactions. PS-[SO$_3$H-PMIM][HSO$_4$] (1mmol, [HSO$_4$]), aromatic compound (20 mmol) and nitric acid (60 mmol) were charged successively into a three-neck flack and stirred at −10 °C for 2 h, then the reaction was allowed to proceed at appropriate temperature for some time. Then the resultant mixture was cooled and diluted with dichloromethane, the catalyst was filtered off and washed with ethanol, and dried. The filtrate was neutralized with 5% sodium bicarbonate solution, and two phases appeared. Took the organic phase out, and dried with anhydrous calcium chloride, and then analyzed it by GC.

Results and Discussion

FT-IR. As shown in Figure 1, for PS-CH$_2$Cl, the characteristic peaks of polystyrene exhibited the C-H stretching vibration of aromatic ring at 3016 cm^{-1}, and C-H asymmetric and symmetric stretching vibrations of methylene at 2920 cm^{-1} and 2855 cm^{-1}. The peaks at 1609 cm^{-1} and 1507 cm^{-1} were due to the C-C skeleton vibration of aromatic ring of polystyrene. Moreover, a typical peak at 1265 cm^{-1} was attributed to stretching vibrations of the functional group -CH$_2$Cl, and another peak at 672 cm^{-1} was due to stretching vibrations of C-Cl.[18] The two typical peaks were practically omitted after introduction of imidazole. Meanwhile, a peak assigned to the C=N stretching vibration of imidazole ring at 1560 cm^{-1} appeared,[12,19] which was indicated the imidazole anchored on the polystyrene by covalent bond. In the IR spectrum of PS-[SO$_3$-PMIM], several strong peaks, *i.e.* 1039 cm^{-1}, 1160 cm^{-1} and 1209 cm^{-1}, appeared which were attributed to the absorb of -SO$_3^-$. When PS-[SO$_3$-PMIM] was acidified with concentrated sulfuric acid, there were no obvious change in IR spectrum but two peaks, 1039 cm^{-1} and 1209 cm^{-1} became stronger, which were attributed to the S=O asymmetric and symmetric stretching vibrations of -SO$_3$- group.

Elements Analysis of PS-CH$_2$-Imidazole and Acidic

Figure 1. IR-spectra of PS-CH$_2$Cl, PS-CH$_2$-imidazole, PS-[SO$_3$-PMIM] and PS-[SO$_3$H-PMIM][HSO$_4$].

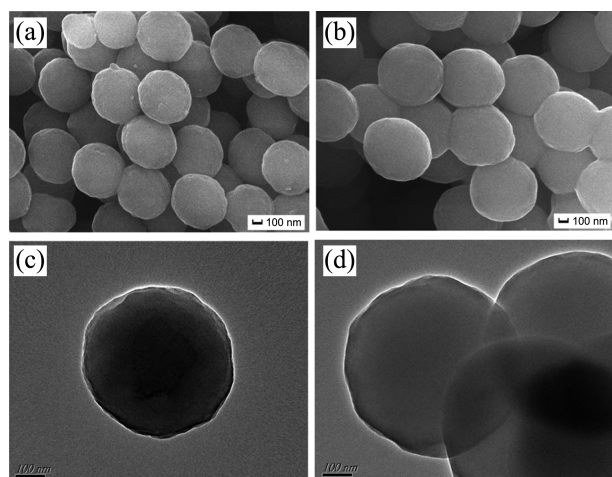**Table 1.** Elemental analysis of PS-CH$_2$-imidazole

Sample	VBC:St:DVB, vol %	% C	% H	% N	Imidazole, mmol/g
PS-CH$_2$-imidazole1	98:0:2	73.88	6.84	12.77	4.56
PS-CH$_2$-imidazole2	74:24:2	74.11	6.88	11.58	4.14
PS-CH$_2$-imidazole3	49:49:2	77.50	7.09	9.24	3.30

"VBC:St:DVB, vol %" was the feed composition of PS-CH$_2$Cl beads. "VBC, St and DVB" were the abbreviation of "4-vinylbenzyl chloride, styrene and divinyl benzene" respectively.

Sites of PS-[SO$_3$H-PMIM][HSO$_4$]. Table 1 showed the elemental analysis for PS-CH$_2$-imidazole. It can be seen that the loading of imidazole in PS-CH$_2$-imidazole increased with increasing of VCB in feed composition of PS-CH$_2$Cl. Acid sites of the PS-[SO$_3$H-PMIM][HSO$_4$] catalyst was confirmed by acid base titration, the loading of [SO$_3$H-PMIM][HSO$_4$] in PS-[SO$_3$H-PMIM][HSO$_4$]1, PS-[SO$_3$H-PMIM][HSO$_4$]2 and PS-[SO$_3$H-PMIM][HSO$_4$]3 were 2.22, 2.03 and 1.69 mmol/g respectively.

SEM/TEM and TG-DSC. It can be seen that PS-CH$_2$Cl (Fig. 2(a) and (c)) was uniform globular in the size of ~600 nm. After the introduction of [SO$_3$H-PMIM][HSO$_4$], the catalyst became big a little, about ~700 nm and the surface became smooth (Fig. 2(b) and (d)), which is in accord with other report.[16]

TG/DSC analysis was carried out in N$_2$ with heating rate of 10 °C/min. As shown in Figure 3, no significant weight loss was observed from both PS-CH$_2$Cl and PS-[SO$_3$H-PMIM][HSO$_4$] at beginning. Above 120 °C, weight loss was accelerated for both the two particles and weight loss speed of PS-CH$_2$Cl was quicker than that of PS-[SO$_3$H-PMIM][HSO$_4$]. There was a obvious weight loss from PS-CH$_2$Cl nearby 150 °C. Correspondingly, for the DSC curve of PS-CH$_2$Cl, a small exothermic peak appeared, however it didn't appear in the DSC curve of PS-[SO$_3$H-PMIM][HSO$_4$]. The weight loss and the exothermic peak of PS-CH$_2$Cl were possibly ascribed to the water inside the porous PS-CH$_2$Cl

Figure 2. SEM and TEM of PS-CH$_2$Cl (a and c) and PS-[SO$_3$H-PMIM][HSO$_4$] (b and d).

Figure 3. TG/DSC curves of PS-CH$_2$Cl and PS-[SO$_3$H-PMIM][HSO$_4$] catalyst.

particles. When the [SO$_3$-PMIM] was immobilized onto PS-CH$_2$Cl in organic solvent, the water was droved and the holes were jammed. When the temperature further increased
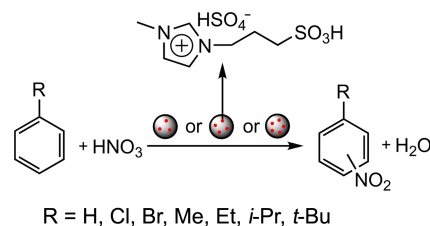

Scheme 2. Mononitration of aromatic compounds.

up to higher than 300 $^{\circ}$C for PS-CH$_2$Cl and 410 $^{\circ}$C for PS-[SO$_3$H-PMIM][HSO$_4$], weight loss accelerated heavily. A possible reason is that their structures were destroyed or the chloromethyl groups and the [SO$_3$H-PMIM][HSO$_4$] separated from PS. The residue weight of PS-[SO$_3$H-PMIM][HSO$_4$] and PS-CH$_2$Cl was about 56.5% and 27.2% at 450 $^{\circ}$C, respectively. These observations indicated that the immobilization of [SO$_3$H-PMIM][HSO$_4$] onto polystyrene could improve the thermal stability of PS-CH$_2$Cl.

Catalytic Reaction. The mononitration of aromatic compounds is showed in Scheme 2.

For the beginning of this study, nitration of toluene with 95% nitric acid catalyzed by PS-[SO$_3$H-PMIM][HSO$_4$] was explored, Table 2 (entry 1-4). The yield of mononitrotoluene was 99%, and the worst product distribution of *ortho-*, *meta-* and *para-*isomers was 52.6:3.8:43.6, which was better than the typical product distribution in the conventional nitration, about 58:4:38.[20] So the new catalyst was efficient and stereoselective. Unfortunately, after the first running, some visible particles were peeled off from PS-[SO$_3$H-PMIM][HSO$_4$] which might attribute to the strong oxidation of concentrate nitric acid. Then, the catalytic activities of PS-[SO$_3$H-PMIM][HSO$_4$] and other various catalysts for nitration of toluene with 68% nitric acid were examined, the results showed in Table 2 (entry 5-10). Obviously, the yield of nitrotoluene over PS-[SO$_3$H-PMIM][HSO$_4$] (entry 5-7) and acidic ionic liquid (entry 8) were much higher than over the support intermediate (entry 9) and no catalyst (entry 10). This meant that the reaction hardly carried out without catalyst and the unprotonated PS-[SO$_3$-PMIM]1 almost had

Table 2. Result of nitration of toluene over various catalyst

Entry	Catalyst	Total selectivity (%)	Yield (%)[c]	Product isomers (%)[d]			*para/ortho*
				ortho	*meta*	*para*	
1[a]	PS-[SO$_3$H-PMIM][HSO$_4$]1	99	99	51.2	4.7	44.1	0.86
2[a]	PS-[SO$_3$H-PMIM][HSO$_4$]2	99	99	50.2	4.2	45.6	0.91
3[a]	PS-[SO$_3$H-PMIM][HSO$_4$]3	99	99	52.6	3.8	43.6	0.83
4[a]	[SO$_3$H-PMIM][HSO$_4$]	99	99	53.9	3.5	42.6	0.79
5[b]	PS-[SO$_3$H-PMIM][HSO$_4$]1	97	75, 74[e], 67[f]	50.2	6.2	40.7	0.81, 0.79[e], 0.71[f]
6[b]	PS-[SO$_3$H-PMIM][HSO$_4$]2	98	72	49.8	5.8	42.0	0.84
7[b]	PS-[SO$_3$H-PMIM][HSO$_4$]3	98	71	52.8	5.7	39.3	0.74
8[b]	[SO$_3$H-PMIM][HSO$_4$]	99	57	56.6	6.2	37.2	0.66
9[b]	PS-[SO$_3$-PMIM]1	99	11	57.5	2.1	40.5	0.70
10[b]	Blank	99	5.3	56.6	3.2	40.2	0.71

[a]95% nitric acid, 45 $^{\circ}$C, 4 h. [b]68% nitric acid, 60 $^{\circ}$C, 7.5 h. [c]Based on crude product. [d]By quantitative GC analysis. [e]Third runs. [f]Fifth runs

Scheme 3. Mechanism of nitration of aromatics over PS-[SO$_3$H-PMIM][HSO$_4$] catalyst.

no catalytic ability. The [SO$_3$H-PMIM][HSO$_4$] and PS-[SO$_3$H-PMIM][HSO$_4$] had obvious catalytic activity. It can be seen that PS-[SO$_3$H-PMIM][HSO$_4$] catalysts exhibited higher catalytic activity and better para-selective than its homogenous counterpart. However, tiny by-products, oxidation products and dinitro-toluene, were produced[21] because of higher reaction temperature and longer reaction time so that the total selectivity of mononitrotoluene decreased a little compare with the total selectivity in entry 1-4. Among the series of PS-[SO$_3$H-PMIM][HSO$_4$] catalysts (entry 5-7), the total yield of nitrobenzene increased with increasing of the loading of [SO$_3$H-PMIM][HSO$_4$], which was attributed to the gradually increasing amount of acid sites in the catalyst. But PS-[SO$_3$H-PMIM][HSO$_4$]2 is the best catalyst with maximum yield and selectivity for 4-nitro toluene.

Two possible catalytic mechanisms of nitration of aromatics over PS-[SO$_3$H-PMIM][HSO$_4$] catalyst were proposed and showed in Scheme 3. The first: nitronium ion carrier was generated by the reaction of HNO$_3$ with activated H$^+$ in PS-[SO$_3$H-PMIM][HSO$_4$]. Electophilic aromatic nitration was

carried out when the nitronium ion carrier attacked the aromatic ring of aromatics. The nitronium ion carrier could not dissociate before reacting with aromatic compounds, and the immobilized ionic liquid carrier was big enough to exhibit stereo-hindrance effect during the reaction so that it was *para*-selective. The stereo-hindrance effect increased with increasing of the loading of [SO$_3$H-PMIM][HSO$_4$], so PS-[SO$_3$H-PMIM][HSO$_4$]2 and PS-[SO$_3$H-PMIM][HSO$_4$]1 afforded better *para*- and *meta*- selective than PS-[SO$_3$H-PMIM][HSO$_4$]3. The second: the HSO$_4^-$ anions in the PS-[SO$_3$H-PMIM][HSO$_4$] could promoted the self-ionization of HNO$_3$ and then nitronium ion carrier was generated.[19] The volume of this kind of nitronium ion carrier was small so that there was little stereo-hindrance effect, so the nitration was often occurred in the *ortho*-position of aromatics because of its high activity. In addition, polystyrene is hydrophobic, but [SO$_3$H-PMIM][HSO$_4$] is hydrophilic, so with the increasing of the loading of [SO$_3$H-PMIM][HSO$_4$] the surface of polystyrene became more and more hydrophilic, which would disadvantage the formation and stable of the nitro-

Table 3. Result for mononitration of substituted benzenes with PS-[SO$_3$H-PMIM][HSO$_4$] catalyst[a]

Entry	R	Catalyst	Temperature (°C)	Yield (%)[b]	Product isomers (%)[c]			para/ortho
					ortho	meta	para	
1	Et	PS-[SO$_3$H-PMIM][HSO$_4$]1	60	67	43.1	7.5	49.4	1.15
		PS-[SO$_3$H-PMIM][HSO$_4$]2		61	40.5	7.6	51.8	1.28
		PS-[SO$_3$H-PMIM][HSO$_4$]3		54	42.3	7.0	50.6	1.20
2	*t*-Bu	PS-[SO$_3$H-PMIM][HSO$_4$]1	60	71	15.1	12.5	72.0	4.77
		PS-[SO$_3$H-PMIM][HSO$_4$]2		70	16.1	12.4	71.0	4.41
		PS-[SO$_3$H-PMIM][HSO$_4$]3		62	15.7	12.5	71.7	4.57
3	*i*-Pr	PS-[SO$_3$H-PMIM][HSO$_4$]1	45	23	22.9	13.4	63.6	2.78
		PS-[SO$_3$H-PMIM][HSO$_4$]2		21	24.7	6.9	68.4	2.77
		PS-[SO$_3$H-PMIM][HSO$_4$]3		21	22.8	8.8	68.4	2.99
4	Br	PS-[SO$_3$H-PMIM][HSO$_4$]1	80	73	36.1	0	63.9	1.77
		PS-[SO$_3$H-PMIM][HSO$_4$]2		72	36.3	0.3	63.4	1.75
		PS-[SO$_3$H-PMIM][HSO$_4$]3		68	34.2	0.1	65.7	1.91
5	Cl	PS-[SO$_3$H-PMIM][HSO$_4$]1	80	52	34.2	-	65.7	1.92
		PS-[SO$_3$H-PMIM][HSO$_4$]2		55	30.3	-	69.6	2.23
		PS-[SO$_3$H-PMIM][HSO$_4$]3		45	41.2	-	58.7	1.42

[a]7.5 h. [b]Based on crude product. [c]By quantitative GC

nium ion carrier. In such microenvironment, the above two nitration process coexisted and competed, which made the *para*-selective decrease and the *meta*- and *para*-selective increase slightly when using PS-[SO₃H-PMIM][HSO₄]1 as catalyst compare with using PS-[SO₃H-PMIM][HSO₄]2.

Results of nitration of other simple aromatic compounds with 68% nitric acid are listed in Table 3. As can be seen, both the three supported ionic liquids could act as effective catalysts and exhibited high activity. The total yield increased with increasing of the loading of [SO₃H-PMIM][HSO₄]. The *para*-selectivity trend of nitration of toluene was not apparent for some substituted benzenes, *i.e.* entry 2 to 4, such substituent groups were often having larger steric hindrance than that of methyl. The essence reason was deserved further studies and the relevant studies would be performed later.

Catalyst Recycle Study. The reusability of PS-[SO₃H-PMIM][HSO₄] catalyst was evaluated in the nitration reaction of toluene with 68% nitric acid catalyzed by PS-[SO₃H-PMIM][HSO₄]1. As shown in Table 2, PS-[SO₃H-PMIM] [HSO₄]1 still showed high activity after third runs. But some insoluble solid particles were found after fourth runs, which might be peeled off from the PS-[SO₃H-PMIM][HSO₄] by long time oxidation of nitric acid so that the PS-[SO₃H-PMIM] [HSO₄] lost efficacy. The catalytic activity decreased 12.9% after fifth runs.

Conclusions

A series PS-[SO₃H-PMIM][HSO₄] catalyst was prepared by grafting [SO₃H-PMIM][HSO₄] to the highly chloromethylated polystyrene beads. It showed a better thermal stability than PS-CH₂Cl resin. It could behave as recyclable solid catalyst for nitration of aromatic compounds with aqueous nitric acid. The total yield of mononitration product increased with increasing of the [SO₃H-PMIM][HSO₄] content. The selectivity of was not only related to the [SO₃H-PMIM][HSO₄] content but also the substituent groups in aromatics.

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