



A novel hydrogen-bonded silica-supported acidic ionic liquid: An efficient, recyclable and selective heterogeneous catalyst for the synthesis of diesters

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MS received 12 August 2017; revised 22 March 2018; accepted 22 March 2018

Abstract. In this study, two novel acidic ionic liquids, including a hydroxyl functionalized diacidic ionic liquid [HFDAIL] and a sulfonated diacidic ionic liquid [SFDAIL], were prepared and immobilized on the surface of silica nanoparticles (SNPs) *via* hydrogen bonding. The materials were characterized by FT-IR, NMR, SEM, nitrogen physisorption measurement, TGA and acid-base titration. The catalytic activity of the prepared catalysts was investigated in the synthesis of phthalate, maleate and succinate diesters under solvent-free conditions. It was found that nanosilica@[HFDAIL] with higher availability of acidic sites and higher hydrophilicity was more efficient compared to the nanosilica@[SFDAIL]. Notably, nanosilica@[HFDAIL] catalyst has also demonstrated excellent selectivity for the diester product while the monoester product was predominant in the case of nanosilica@[SFDAIL] even after prolonged reaction time or higher catalyst loading. In addition, the nanosilica@[HFDAIL] catalyst could be separated by simple filtration and reused several times without any significant loss of catalytic performance, but a remarkable decrease in activity was observed for nanosilica@[SFDAIL] in the next runs.

Keywords. Supported ionic liquids; hydrogen bonding; phthalate diesters; selectivity; diesterification.

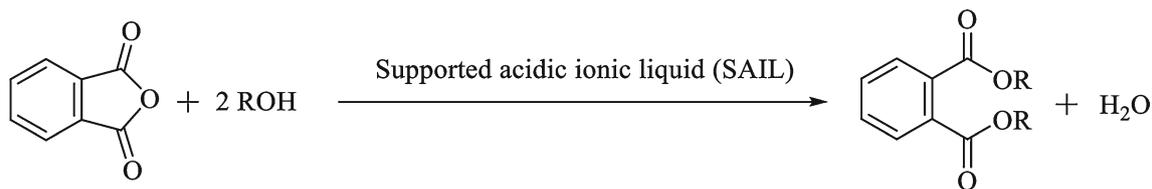
1. Introduction

Aliphatic and aromatic esters important organic compounds, which are generally used as solvents, perfumes and also as precursors for pharmaceuticals, agrochemicals and fine chemicals.¹ Particularly, there has been increasing interest for the synthesis of diester product which is employed as plasticizers in many industrial applications. Usually, esters are obtained by the esterification of alcohols with carboxylic acids² in the presence of inorganic liquid acids,³ solid acids⁴ or bioenzymes⁵ as conventional catalysts. However, the application of conventional homogeneous acid catalysts in the synthesis of esters has been restricted today because of the difficulty in the waste neutralization, separations, reactor corrosion, and reusability. On the other hand, the use of solid acid catalysts in this reaction has typically resulted in lower catalytic performance because

these systems suffer from some limitations such as steric hindrance of bulky support and its mass transfer problem, low interaction of reactants with active sites and low catalyst distribution in the reaction media as well as the leaching of active sites during the course of the reaction. Consequently, there is much room to develop more improved catalytic systems for esterification reaction which may integrate the interesting features of both homogeneous and heterogeneous systems.⁶⁻⁸ In this context, the immobilization of acidic molecules on the high surface area nano-sized supports is one of the interesting research directions along the avoiding deterrent effect of bulky supports. Also, along this research line, acidic ionic liquids as a key sub-class of ionic liquid-tagged catalysts, with organic skeleton and thus improved interaction with substrates as well as enhanced acidity, have attracted enormous attention in recent years in the acid catalyzed organic transformation.

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Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-018-1454-z>) contains supplementary material, which is available to authorized users.



Scheme 1. Esterification of phthalic anhydride with alcohols using synthesized supported ionic liquids.

The room temperature ionic liquids (RTILs) are environmentally friendly solvents and catalysts, and have adjustable physical and chemical properties. These compounds have received broad attention of researchers from various fields such as synthesis, catalysis, separation and electrochemistry.^{9–13} Their favorable properties, such as high thermal stability, negligible vapor pressure, tunable acidity and strong dissolvability provide good opportunities to ionic liquids for specific purposes.^{14–18} However, many of ionic liquids are relatively expensive or toxic thus employing the ionic liquids in an unrecoverable form results in crucial economic and environmental shortcomings. In addition, the high viscosity of the ILs can induce mass transfer limitations. If the chemical reaction is fast, only a minor part of the IL contributes to the reaction, known as “diffusion layer”.¹⁹ In addition, product separation and catalyst recovery were proven to be difficult in homogeneous reactions.²⁰ Therefore, the heterogenization of ILs on a solid support is highly desirable and the concept of supported ionic liquid catalysis (SILC)²¹ has been recently developed to combine the advantages of ILs and recoverable acid catalysts.^{22–26} Among the varied approaches developed for the immobilization of ILs on a solid support, covalent immobilization has been considered as the major method in the literature since it provides a versatile and strong anchoring of IL to support thus avoids the leaching of IL under reaction conditions. In this context, less attention has been paid to other chemical immobilization methods such as hydrogen bonding. Here, we tried to develop novel supported acidic IL systems by emphasizing on hydrogen bonding immobilization. We believe that immobilization of IL *via* hydrogen bonding may increase the accessibility of active sites and facilitate the immobilization process since it can be achieved under milder reaction condition.

In recent years, the application of various immobilized ionic liquids in esterification reaction has received more consideration. In 2011, Miao *et al.*, reported the use of acidic IL on silica gel for esterification.²⁷ In 2013, Shao *et al.*, used an immobilized Brønsted acidic IL catalyst on chloromethyl polystyrene grafted silica gel for esterification reaction.²⁸ Despite the remarkable

achievements using these systems in terms of activity, the main challenge of this transformation is the selective formation of diester product which has not been addressed properly in the previous studies; almost all catalytic systems gave monoester compound as the final product. Due to importance and various applications of phthalate diesters in different industries and in continuation of our studies on the synthesis and application of various ionic liquids,^{29–35} herein we report the synthesis of two novel supported ILs, [HFDAIL] and [SFDAIL], *via* hydrogen bonding immobilization and compare their catalytic performance in the preparation of phthalate diesters under solvent-free conditions (Scheme 1).

2. Experimental

2.1 Material and methods

All the solvents and chemicals were commercially purchased from Merck and Fluka and used without further purification. IR measurements were performed on a Nicolet 800 instrument using KBr or liquid film. ¹H NMR spectra were recorded on a Bruker DRX500 (500 MHz) and ¹³C NMR spectra on a Bruker DRX500 (125 MHz) spectrometer in DMSO and D₂O, respectively, and calibrated with tetramethylsilane (TMS) as the internal reference. Quantitative product analysis was conducted by gas chromatography on Hewlett Packard HP-5890 instrument equipped with HP-1 column (30 m long, 0.5 mm diameter), and flame ionization detector (FDI), using N₂ as carrier gas at a flow rate of 2 mL min⁻¹. Scanning electron microscope (SEM) images of the samples were examined on a Philips XL-30 ESEM instrument. The N₂ adsorption/desorption isotherms were measured using a Micromeritics Tristar II 3020 instrument. The nanosilica support (Fumed silica S5130 purchased from Sigma Chemical Co.) was dried at 250 °C for 6 h before use. All the solvents used were strictly dried according to standard operations and stored over 4 Å molecular sieves.

2.2 Preparation of supported IL catalysts

2.2a Preparation of hydroxyl and sulfonic acid functionalized diacidic ionic liquids: 2.2.1a Preparation

of 2,2-bis((3-methylimidazolidin-1-yl) methyl) propane-1,3-diol bromide salt (IL-Br): A mixture of 1-methylimidazole (6.25 mmol, 0.5 mL) and 0.65 g of 2,2-bis(bromomethyl)-1,3-propanediol (2.5 mmol) was heated at 150 °C for 8 h under magnetic stirring. After cooling to room temperature, the obtained solid was washed three times with acetonitrile and the residue was dried in an oven at 100 °C for 2 h, giving IL-Br as a white powder (yield: 95.25 %, M.p.: 150 °C). ¹H NMR (DMSO-d₆): δ 3.24 (4H, s, CH₂N), 3.84 (6H, s, CH₃), 4.31 (4H, s, CH₂OH), 4.72 (2H, s, OH), 7.42 (4H, dd, *J* = 10 Hz, *J* = 5 Hz, CH = CH) and 8.72 (2H, s, NCHN) ppm; ¹³C NMR (DMSO-d₆): δ 35.94, 45.21, 48.58, 58.48, 123.72, 123.86 and 137.38 ppm; FT-IR (KBr) ν_{max}: 621, 771, 830, 1061, 1165, 1451, 1573, 1760, 1656, 2935 and 3261 cm⁻¹.

2.2.1b Preparation of 3,3'-(2,2-bis((sulfoxy) methyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) bromide [SFDAIL]: The sulfonic acid-functionalized ionic liquid, was prepared by nucleophilic substitution reaction of IL-Br salt with chlorosulphonic acid. To do this, 0.8 g of IL-Br salt (2 mmol) was dissolved in acetonitrile. Then 0.5 mL of chlorosulphonic acid (8 mmol) was added slowly at room temperature. Then, the mixture was stirred for 4 h at the same temperature. The reaction mixture was filtered to give yellow precipitate. It was washed with toluene three times and dried under vacuum at 100 °C for 1 h, giving SFDAIL as a yellow solid (yield: 97.5%). ¹H NMR (DMSO-d₆): δ 3.33 (4H, s, CH₂N), 3.47 (6H, s, CH₃), 4.04 (4H, s, CH₂OH), 5.33 (2H, s, SO₃H), 7.06 (4H, d, *J* = 5 Hz, CH = CH) and 8.30 (2H, s, NCHN) ppm; ¹³C NMR (DMSO-d₆): δ 36.19, 43.83, 48.27, 63.89, 123.88, 124.26 and 137.79 ppm; FT-IR (KBr) ν_{max}: 587, 783, 1019, 1252, 1459, 1585, 1709 and 3160 cm⁻¹.

2.2.1c Preparation of 3,3'-(2,2-bis(hydroxymethyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) hydrogen sulfate [HFDAIL]: The hydroxyl functionalized ionic liquid was prepared by anion exchange of IL-Br salt. 0.5 g (1.2 mmol) of IL-Br salt, obtained in the first stage, was dissolved in methanol (30 mL) under stirring. After that, the system was slowly heated up to 60 °C in an oil bath. Then, 0.13 mL of sulfuric acid (2.4 mmol) was added drop-wise and stirred for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The resultant material was washed with dichloromethane (3 × 5 mL) and then dried under vacuum at 100 °C for 2 h to afford HFDAIL as yellow viscous oil liquid in 95% yield. ¹H NMR (DMSO-d₆): δ 3.20 (4H, s, CH₂N), 3.81 (6H, s, CH₃), 4.27 (4H, s, CH₂OH), 4.74 (2H, s, OH), 7.39 (4H, dd, *J* = 10 Hz, *J* = 5 Hz, CH = CH) and 8.69 (2H, s, NCHN) ppm; ¹³C NMR (DMSO-d₆): δ 36.73, 44.97, 49.63, 59.53, 124.31, 124.58 and 138.73 ppm; FT-IR (KBr) ν_{max}: 590, 776, 880, 1054, 1223, 1458, 1572, 1642, 2510, 3096 and 3329 cm⁻¹.

2.2b Immobilization of [HFDAIL] onto the silica nanoparticles: Silica nanoparticles were dried in an oven at 250 °C for 6 h. In a round bottom flask, 0.75 g of nanosilica

was dispersed in dry methanol (15 mL). The [HFDAIL] ionic liquid (0.25 g) was dissolved in hot methanol (10 mL) and added slowly into the prepared mixture. After that, the mixture was stirred at room temperature for 24 h. Upon completion of the process, the solvent (methanol) was evaporated under reduced pressure. Finally, the resulting solid was washed with acetone (2 × 10 mL) and dried under vacuum at 70 °C for 5 h to give nanosilica-supported hydroxyl-functionalized diacidic ionic liquid (nanosilica@[HFDAIL]) as a white powder.

2.2c Immobilization of [SFDAIL] onto the silica nanoparticles: Silica nanoparticles were dried in an oven at 250 °C for 6 h. In a round bottom flask, 1.5 g of nanosilica was dispersed in dry methanol (15 mL). The [SFDAIL] ionic liquid (0.5 g) was dissolved in hot methanol (10 mL) and added slowly into the prepared mixture. After that, the mixture was stirred at room temperature for 24 h. Upon completion of the process, the solvent (methanol) was evaporated under reduced pressure. Finally, the resulting solid was washed with acetone (2 × 10 mL) and dried under vacuum at 70 °C for 5 h to give nanosilica supported sulfonated diacidic ionic liquid (nanosilica@[SFDAIL]) as a white powder.

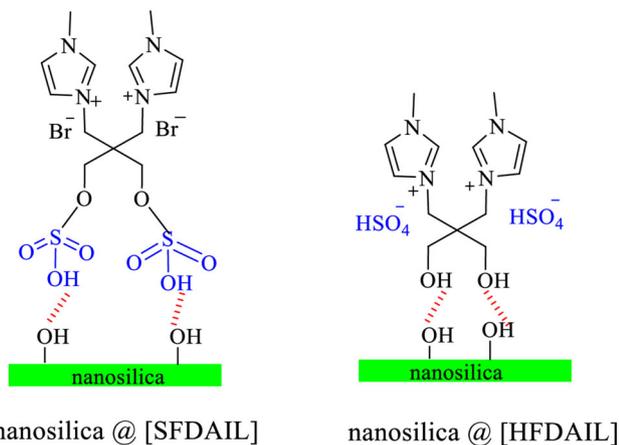
2.3 Typical procedure for the esterification reaction with nanosilica@[HFDAIL]

The typical procedure for esterification of phthalic anhydride with butanol as an example, was performed as follows: phthalic anhydride (1 mmol, 0.15 g), butanol (5 mmol, 0.46 mL, 0.37 g) and nanosilica@[HFDAIL] as catalyst (10 mol% to phthalic anhydride, 0.05 g) were poured into a 50 mL round bottom flask equipped with a dean-stark apparatus, reflux condenser and a magnetic stirrer. Then the mixture was stirred at 125 °C for 8 h. The completion of reaction was monitored by TLC using (EtOAc/Hexane 2:8) as eluent. After completion of the reaction as indicated by TLC, ethyl acetate was added to dissolve the product and then the reaction mixture was filtered to separate the catalyst from the reaction mixture. Then, ethyl acetate was evaporated under vacuum to afford the desired product as yellow oil liquid at 92% yield (0.25 g, B.p.: 340 °C). The obtained product (dibutyl phthalate) was subjected to drying under vacuum at 70 °C for 5 h. The solid catalyst was washed with acetone to remove the residual product and dried under vacuum at 70 °C.

3. Results and Discussion

3.1 Catalyst characterization

For the preparation of supported acidic ILs, [HFDAIL] and [SFDAIL] were initially synthesized using readily available or pre-synthesized precursors. Then, the prepared acidic ILs were immobilized onto the nanosilica *via* hydrogen bonding of either sulfonic acid or hydroxyl group in ILs with surface hydroxyl group of



Scheme 2. The prepared supported acidic ionic liquids *via* hydrogen bonding.

nanosilica in methanol for 24 h at room temperature to give nanosilica@[HFDAIL] and nanosilica@[SFDAIL] (Scheme 2).

After synthesis and immobilization of acidic ILs on the surface, the structure of the prepared catalysts were analyzed by various techniques. Determining density of acidic groups in the nanosilica@[HFDAIL] and nanosilica@[SFDAIL] by titration with NaOH, showed that the

amount of H^+ loading in the catalysts are 1 mmol/g and 0.5 mmol/g, respectively.

3.1a FT-IR: To confirm the immobilization of ILs on the nanosilica support, FT-IR spectra were recorded (Figure 1). The characteristic peaks of pure ionic liquid [SFDAIL], around 3160 cm^{-1} , 1709 cm^{-1} , 1584 cm^{-1} and 1458 cm^{-1} were clearly observed in Figure 1a, which are attributed to the O-H stretching vibration of the $-SO_3H$ group and C=N, C=C stretching vibrations of the imidazole ring, respectively. The peaks at 1251 cm^{-1} and 1186 cm^{-1} were assigned to the S=O asymmetric and symmetric stretching vibrations of the $-SO_3H$ group. In the FT-IR spectra of the nanosilica sample (Figure 1b), the Si-O stretching vibration of the nanosilica could be observed as a strong peak at 808 cm^{-1} and 1101 cm^{-1} . Moreover, the peak centered at 456 cm^{-1} was due to Si-O-Si bending vibration and a broad feature was seen at 3400 cm^{-1} belonging to the Si-OH groups and adsorbed water in nanosilica.

In the FT-IR spectra of nanosilica-supported acidic ILs (Figure 1c and 1d), apart from the main peaks of nanosilica, additional peaks attributed for the functional groups of the [SFDAIL] and [HFDAIL] were also

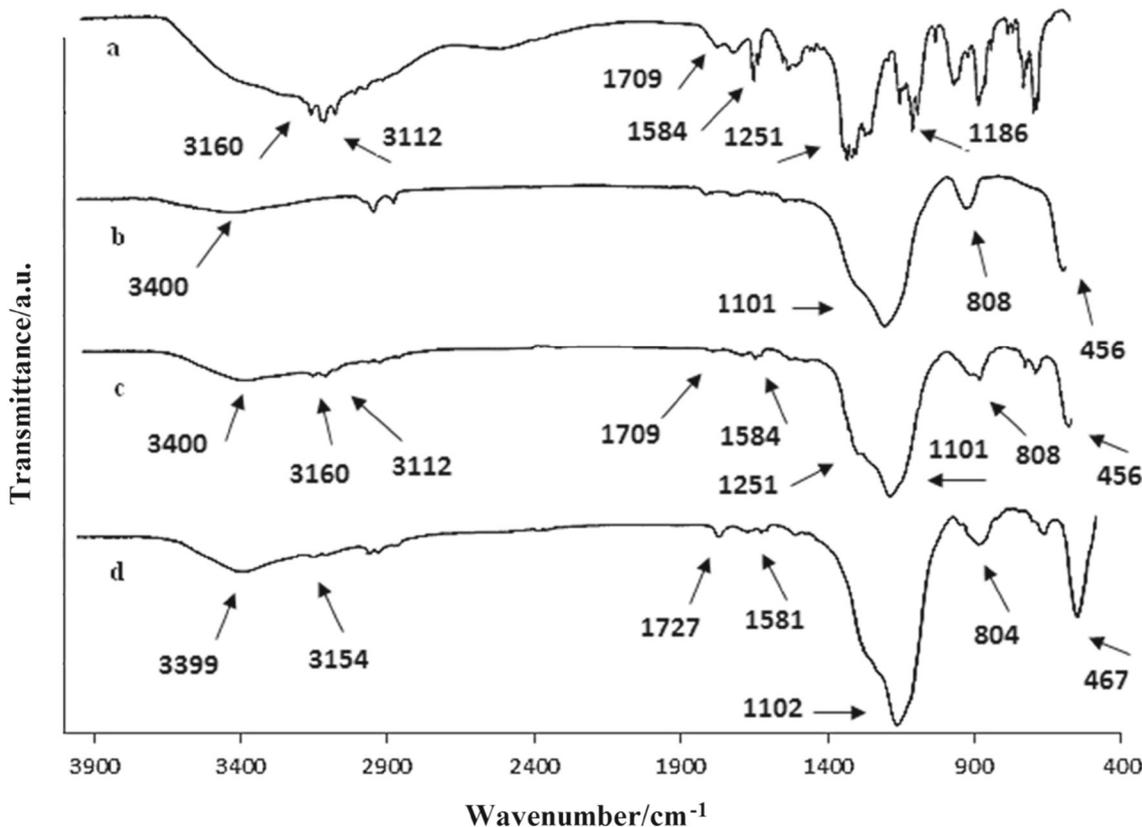


Figure 1. FT-IR spectra of (a) pure ionic liquid [SFDAIL], (b) nanosilica, (c) nanosilica@[SFDAIL] and (d) nanosilica@[HFDAIL]. The spectra are vertically shifted for clarity.

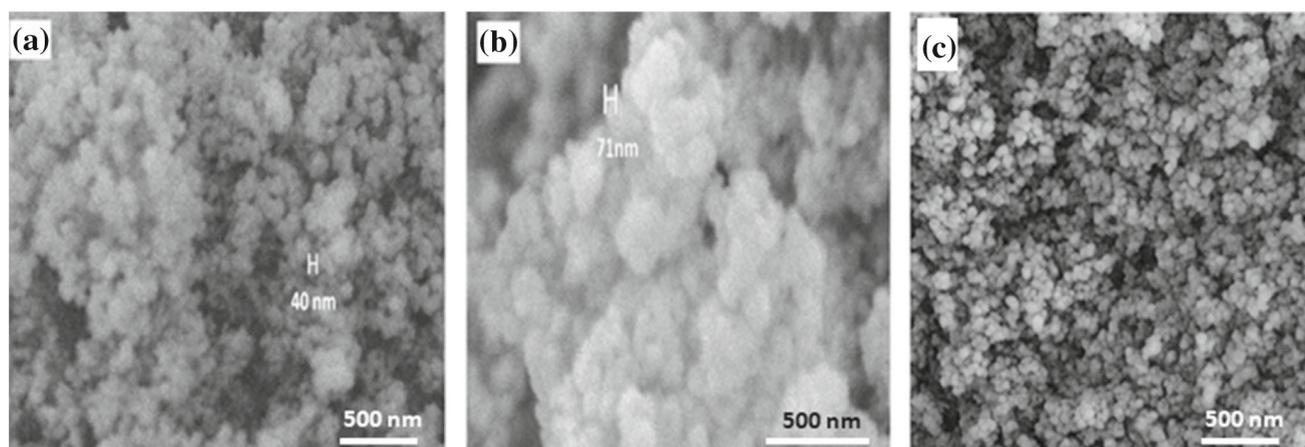


Figure 2. SEM images of (a) nanosilica, (b) nanosilica [HFDAIL] and (c) anosilica@[SFDAIL].

observed, but, as expected, the intensity of the peaks decreased significantly. This observation clearly confirms that the both ILs have successfully supported onto the surface of the nanosilica. As shown in Figures 1c and 1d, the intensity of peak centered at about 3400 cm^{-1} (corresponding to the Si-OH band and adsorbed water in nanosilica) in the nanosilica@[HFDAIL] is relatively higher than that of nanosilica@[SFDAIL]. This observation might be responsible for the higher hydrophilicity of nanosilica@[HFDAIL] than nanosilica@[SFDAIL].

3.1b SEM: The shape and surface morphology of the samples were characterized by SEM technique. SEM images for typical nanosilica samples before and after ILs supporting are shown in Figure 2. It should be noted that the morphological homogeneity is maintained after supporting of ILs which demonstrates that the particles of nanosilica have a good mechanical stability during the supporting process. The SEM images also reveal that nanosilica support contains nanoparticles with the size of less than 50 nm (Figure 2a). Comparing the images of Figure 2a with 2b and 2c shows that no obvious aggregation of the silica nanoparticles was detected after immobilization of ILs.

3.1c TG: TG analysis was conducted in the range of 25–900 °C under nitrogen atmosphere to investigate the thermal stability and organic content of the catalysts. As shown in Figure S1 (a and b) in Supplementary Information, both materials demonstrated remarkable weight loss above 200 °C, which corresponds to the supported ILs on nanosilica. Loading of ILs (wt%) was calculated as shown in Figure S1 in Supplementary Information. Based on TG curves (Figure S1 a' and b'), it was concluded that the amount of loaded ILs on the solid support is about 29% and 33% for nanosilica@[HFDAIL] and nanosilica@[SFDAIL],

respectively. Furthermore, TG analysis revealed that despite the immobilization of ionic liquid on the support *via* hydrogen bonding which is weaker than covalent bonding, ionic liquids are remarkably stable on the solid support up to about 200 °C. Furthermore, as indicated in DTG curves (Figure S1 a'' and b''), maximum weight loss in both materials is centered about 380 °C. This observation strongly confirms that major content of IL is still stable on the support up to 380 °C (Figure S1 in Supplementary Information).

3.1d N_2 adsorption-desorption: The specific surface area and average pore diameter of the prepared materials were studied by the N_2 adsorption-desorption isotherms (Figure 3). Results showed that both samples pure nanosilica and nanosilica@[HFDAIL] possess type-IV isotherms with a H_3 hysteresis loop centered at relative pressure of about 0.4–0.8, confirming the ordered mesoporous structure of the materials (Figures 3a, 3b). Also, according to BJH calculation, pore diameter for the nanosilica and nanosilica@[HFDAIL] was 20 and 18 nm, respectively, corroborating the mesoporous and regular pore structure of the materials (Figures 3c, 3d). The data obtained from N_2 adsorption-desorption experiments of pure nanosilica and nanosilica@[HFDAIL] are summarized in Table 1, in which the Brunauer–Emmett–Teller (BET) surface area of the supported ionic liquid on nanosilica was found to be remarkably lower than that of corresponding mesoporous nanosilica (Figures 3e, 3f). These data indicate that the ionic liquid was successfully immobilized onto the nanosilica.

3.2 Catalytic activity of supported ILs in esterification reaction of different alcohols with anhydrides or succinic acid

In order to evaluate the catalytic activity of the prepared catalysts, the esterification of n-butanol with phthalic

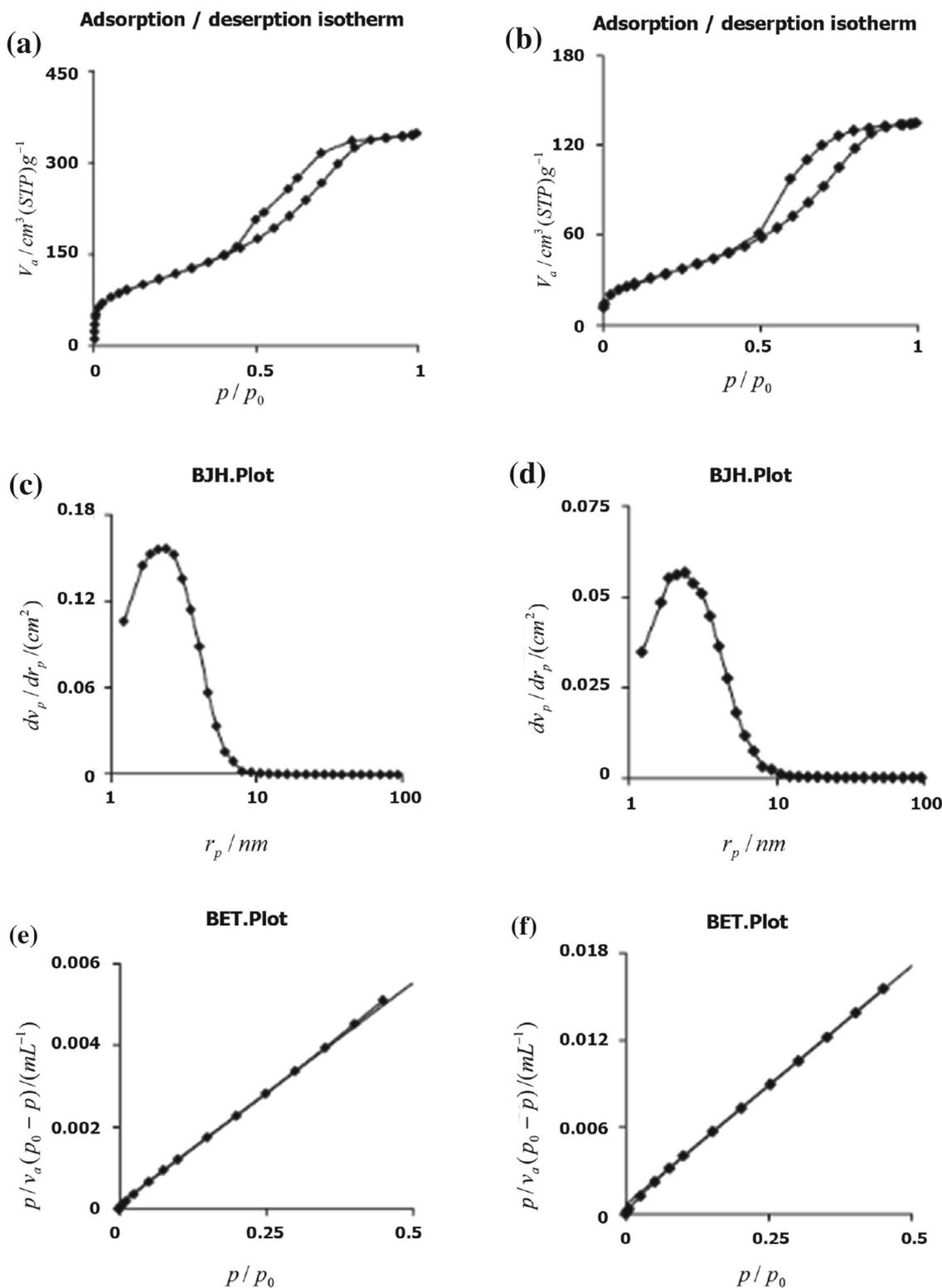


Figure 3. N_2 adsorption/desorption isotherms of (a) pure nanosilica and (b) nanosilica@[HFDAIL], BJH plots of (c) pure nanosilica and (d) nanosilica@[HFDAIL], BET plots of (e) pure nanosilica and (f) nanosilica@[HFDAIL].

anhydride was tested with nanosilica@[HFDAIL] and nanosilica@[SFDAIL] under solvent-free condition at 120 °C. As can be seen in Table 2, entries 1 and 2,

while the nanosilica@[HFDAIL] demonstrated complete conversion and excellent selectivity for diester compound, lower conversion (even after prolonged

Table 1. Results of N₂ adsorption-desorption measurements of nanosilica and nanosilica@[HFDAIL].

Samples	S _{BET} (m ² g ⁻¹) ^a	D (nm) ^b
Pure nanosilica	399	20
nanosilica@[HFDAIL]	13	18

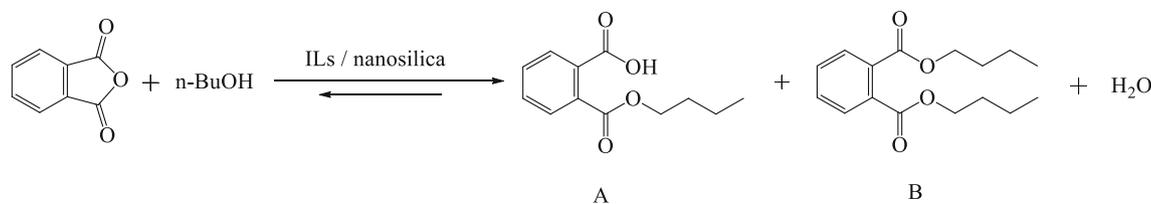
^aBET surface area calculated using N₂ adsorption-desorption measurements; ^bMean pore diameter calculated using BJH method from adsorption branch of N₂ adsorption-desorption isotherm.

reaction time) and higher selectivity for monoester product was obtained in the case of nanosilica@[SFDAIL], using 10 mol% of each catalyst under other same reaction conditions. Surprisingly, increasing the catalyst loading to 20 mol% in the case of nanosilica@[SFDAIL] resulted in complete conversion in the reaction within 15 h, but the monoester compound was still the major product in these circumstances (Table 2, Entry 3). The higher catalytic activity as well as improved selectivity toward the diester compound in the case of nanosilica@[HFDAIL] might be attributed to both its higher availability of acidic sites (as counter ion of IL) and its higher hydrophilicity, compared to the nanosilica@[SFDAIL] catalyst. Considering the higher hydrophilicity of nanosilica@[HFDAIL] when compared with nanosilica@[SFDAIL] as well as relatively higher hydrophobicity of diester product compared to monoester one, we hypothesize that the retention time of monoester compound in the pore surface of nanosilica@[HFDAIL], where the catalytic sites are located, is longer; thus, the monoester compound is not

expelled from the channels until it is converted to the more hydrophobic diester product. Notably, the catalytic performance of nanosilica@[HFDAIL] was comparable, even higher, than that of homogeneous HFDAIL in both terms of activity and selectivity (Table 2, Entries 1 and 4). This may be a strong evidence to the fact that, being the counter ion of IL, acidic groups in the nanosilica@[HFDAIL] is completely exposed and available to the substrates like a homogeneous catalytic system.

In the next step, to obtain appropriate conditions for esterification of phthalic anhydride with alcohols, effect of the reaction temperature and time, amount of catalyst and molar ratio of phthalic anhydride to butanol were investigated in the presence of nanosilica@[HFDAIL] as the selective catalyst. The results are shown in Table 3. As shown in Table 3, the optimum conditions is 125 °C, 10 mol% catalyst and molar ratio of phthalic anhydride to butanol 1:5 (Table 3, entry 5).

In order to evaluate the scope and limitations in the catalytic performance of nanosilica@[HFDAIL], esterification reaction of different alcohols with phthalic and maleic anhydrides as well as succinic acid was carried out. The results are summarized in Table 4. Generally, it could be found that nanosilica@[HFDAIL] showed very high catalytic performance for esterification reactions of a wide range of substrates and in all cases the diester product was selectively formed. As shown in Table 4, good to excellent yields ranging from 56 to 100% with perfect conversion (100%) of phthalic or maleic anhydride and succinic acid were obtained in all systems under investigation. According to Table 4 (entries 3 to 5), esterification of long alkyl chain alcohols was very

Table 2. Comparison of catalytic performance of ILs/nanosilica in the esterification reaction of phthalic anhydride with butanol.^a

Entry	Catalyst	Catalyst (mol %)	PhA Conv. (%)	Time (h)	Yield (%)	
					A	B
1	nanosilica@[HFDAIL]	10	100	8	8	92
2	nanosilica@[SFDAIL]	10	65	24	88	12
3	nanosilica@[SFDAIL]	20	100	15	67	33
4	[HFDAIL]	10	100	8	25	75

^aReaction conditions: The molar ratio of butanol to phthalic anhydride = 5:1; T = 125 °C.

Table 3. Optimization of reaction conditions^a for the esterification reaction of phthalic anhydride with butanol in the presence of nanosilica@[HFDAIL].

Entry	Catalyst (mol%)	(PA:BuOH)	Temperature (°C)	Time (h)	Yield (%) ^b
1	10	1:5	25	24	0
2	10	1:5	50	24	3
3	10	1:5	75	10	30
4	10	1:5	100	10	70
5	10	1:5	125	8	92
6	10	1:5	150	2	63
7	5	1:5	125	9	75
8	15	1:5	125	8	90
9	10	1:2	125	10	70
10	10	1:3.5	125	9	80
11	10	1:6.5	125	8	90

^aReaction conditions: reaction was carried out under solvent-free conditions; ^bYields refer to the diester products (GC yield).

satisfactory due to their high boiling points. Esterification reactions of 2-methoxy ethanol and allyl alcohol showed good results too (Table 4, entries 6 and 7). Esterification of methanol and ethanol (entries 1 and 2) gave lower yields compared with other alcohols due to their lower boiling points. Esterification reaction of maleic anhydride with alcohols also provided very satisfactory results (Table 4, entries 8 and 9). Since succinic acid has lower steric hindrance compared with phthalic and maleic anhydrides in the reaction center (carbonyl carbon), thus it demonstrated better results in esterification reaction (Table 4, entries 10 and 11). Satisfied with these significant achievements, we then checked the ability of the catalyst for esterification of butandiol and 1,2,6-hexanetriol with PA. However, no product was achieved in these reactions even at elevated temperatures (Table 4, entries 12 and 13). It seems that a polymer was produced instead of the cyclic diester in these cases. Again, for comparison purposes, we checked the esterification reactions of phthalic anhydride with 2-ethylhexyl alcohol or butanol in the presence of [HFDAIL] instead of nanosilica@[HFDAIL] as the catalyst. These reactions indicated 100% and 95% yield of diester, respectively, with 100% conversion of phthalic anhydride. Thus, it is significant that the nanosilica@[HFDAIL] exhibited similar catalytic activity as its homogeneous counterpart.

3.3 Reusability of the catalyst

Since the recoverability of the supported catalyst is very important issue from both economic and environmental viewpoints, we next checked the reusability of the nanosilica@[HFDAIL] catalyst in the

esterification of phthalic anhydride and butanol as a model reaction. To do this, the nanosilica@[HFDAIL] catalyst was simply filtered from the reaction mixture and checked for the next run. As can be seen in Figure 4, the recovered catalyst could be reused for at least 7 times without significant loss of catalytic activity. The successful recovery of the catalyst from such reaction accomplishing under harsh condition, despite the immobilization of IL *via* hydrogen bonding, highlights the notion that the developed immobilization approach in this study not only provides high catalytic activity of supported acidic groups, like its homogeneous counterpart, but it also ensures the stability and recoverability of the catalyst under the described reaction conditions. For comparison purpose, we also checked the recoverability of the other catalyst, nanosilica@[SFDAIL], in the same transformation. Unexpectedly, we found that the activity of this catalyst was significantly dropped in the subsequent runs under the same reaction conditions. Although the exact reason for this observation is unclear for us, we think that the catalytic and immobilization sites in this catalyst being same is responsible for loss of its performance.

Finally, the catalytic performance of nanosilica@[HFDAIL] was compared with previous literature reports about application of various ionic liquids for esterification reaction. As can be seen in Table 5, the nanosilica@[HFDAIL] demonstrated comparable or better, in most cases, catalytic activity than the other catalysts. Lower catalyst loading, higher selectivity toward the diester product and, most importantly, the recoverability and stability of nanosilica@[HFDAIL] are the main advantages of this system in comparison with previous catalysts.

Table 4. Esterification reaction of anhydride and succinic acid with different alcohols catalyzed by nanosilica@[HFDAIL].^a

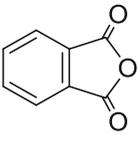
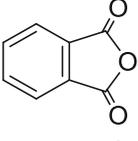
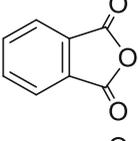
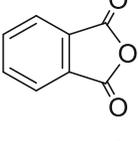
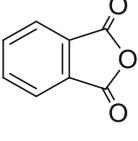
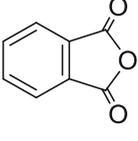
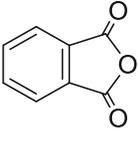
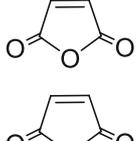
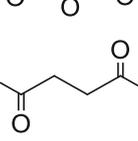
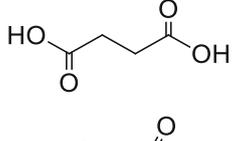
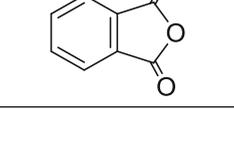
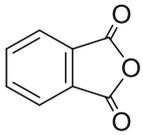
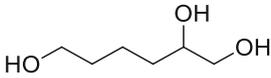
Entry	Anhydride or Acid	Alcohol	Temperature (°C)	Time (h)	Yield (%) ^b
1		CH ₃ OH	65	24	56
2		EtOH	78	24	70
3		HO-CH ₂ -CH ₂ -CH ₃	98	10	82
4		HO-CH ₂ -CH ₂ -CH ₂ -CH ₃	118	8	92
5		HO-CH ₂ -CH(CH ₂ CH ₃)-CH ₂ -CH ₂ -CH ₃	180	3	100
6		HO-CH ₂ -CH=CH ₂	97	7	72
7		HO-CH ₂ -CH ₂ -O-CH ₃	125	6	68
8		HO-CH ₂ -CH(CH ₂ CH ₃)-CH ₂ -CH ₂ -CH ₃	180	1	100
9		HO-CH ₂ -CH=CH ₂	97	8	95
10		HO-CH ₂ -CH ₂ -CH ₂ -CH ₃	118	2	100
11		HO-CH ₂ -CH=CH ₂	97	6	100
12		HO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	235	5	-

Table 4. (contd.)

Entry	Anhydride or Acid	Alcohol	Temperature (°C)	Time (h)	Yield (%) ^b
13			178	5	-

^aReaction conditions: anhydrides or acid: alcohol: nanosilica@[HFDAIL] = 1:5:0.1; ^bYields refer to the diester products (GC yield).

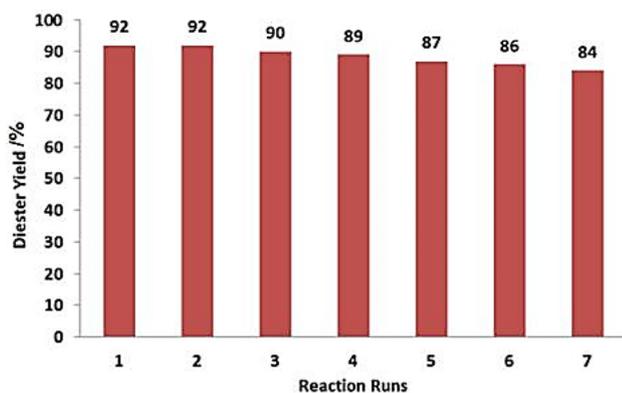


Figure 4. Reusability of nanosilica@[HFDAIL] catalyst for esterification of phthalic anhydride with butanol under optimized reaction condition.

4. Conclusions

In summary, we developed a novel approach in supported ionic liquid catalysis by design of new supported ionic liquids *via* hydrogen bonding. Using this strategy, two novel acidic ionic liquids including a hydroxyl functionalized diacidic ionic liquid [HFDAIL] and a sulfonated diacidic ionic liquid [SFDAIL], were prepared and immobilized on the surface of silica nanoparticles (SNPs) *via* hydrogen bonding. The catalytic activity of the prepared catalysts was investigated in the synthesis of phthalate, maleate and succinate diesters under solvent-free conditions. It was found that nanosilica@[HFDAIL] with higher availability of acidic sites and higher hydrophilicity

Table 5. Comparison of catalytic activity of nanosilica@[HFDAIL] with other reported catalysts in various esterification reactions.

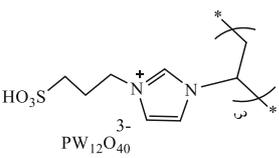
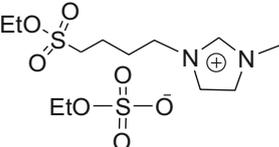
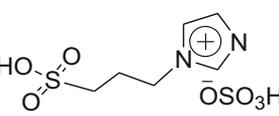
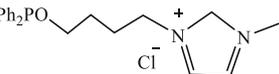
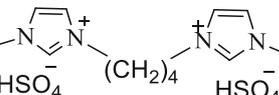
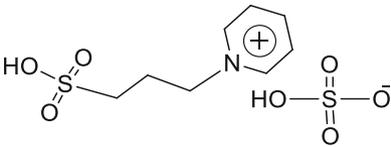
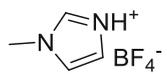
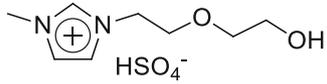
Entry	Catalyst	Catalyst (mol%)	(Acid:Alcohol)	T (°C)	Time (h)	Conv. (%)	Yield (%)	Ref.
1 ^a		11	1:4	130	3	96.4	-	36
2		20	1:2	80	4	-	70	37
3		5	1:2.5	120-130	1.5	98	-	38
4		Excess	1:2	100	3.5	-	78	39
5 ^a		17	1:4	60	4	-	74	40

Table 5. (contd.)

Entry	Catalyst	Catalyst (mol%)	(Acid:Alcohol)	T (°C)	Time (h)	Conv. (%)	Yield (%)	Ref.
6		15	1:2.5	115-125	1.5	95	-	41
7		Excess	1:2	110	4	>99	-	42
8		Excess	1:2	80	18	50	99	43
9	nanosilica@[HFDAIL]	10	1:5	125	8	100	92	This work
10	nanosilica@[SFDAIL]	10	1:5	125	24	80	12	This work

^aMonoester was formed as the main product.

was more efficient when compared with the nanosilica@[SFDAIL]. Notably, nanosilica@[HFDAIL] catalyst has also demonstrated excellent selectivity for diester product while the monoester product was predominant in the case of nanosilica@[SFDAIL] even after prolonged reaction time or higher catalyst loading. In addition, the nanosilica@[HFDAIL] catalyst could be separated by simple filtration and reused several times without any significant loss of catalytic performance, but a remarkable decrease in activity was observed for nanosilica@[SFDAIL] in the subsequent runs. Beside the introduction of new concept in supported acidic ionic liquids and development of an efficient method for selective synthesis of diester plasticizers, this study suggests some advantages such as easy work-up process, clean reaction condition, high reactivity for various substrates, outstanding reusability and stability of the catalyst with small decrease in their catalytic activity and good thermal stability. These outstanding features would make this study attractive for many researchers such as those who work on supported ionic liquid systems, synthesis of plasticizers or green chemistry developers.

Supplementary Information (SI)

Electronic Supplementary Information (ESI) available are FT-IR, NMR spectra, TGA curves, N₂ adsorption/desorption isotherms, BJH plots, BET plots, SEM images, etc. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

The financial assistance from the Malek-Ashtar University of Technology (MUT), Tehran, Iran, is gratefully acknowledged.

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