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Catalysis Today 131 (2008) 98–103

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Acylation of sulfonamines using silica grafted 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium ionic liquids as catalysts

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Abstract

Heterogeneous immobilized ionic liquid catalysts were prepared via grafting of 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate or bis{(trifluoromethyl)sulfonyl} imide ($[NTf_2]^-$) on silica supports with different surfaces and pore size. In addition to the adsorption–desorption isotherms of nitrogen at −196 °C, the catalysts were characterized by TG-DTA, XPS, DRIFTS, DR-UV–vis, NMR, and XRD techniques. The catalytic behavior was checked in the acylation of three different sulfonamines: benzenesulfonamine, *p*-nitrobenzene-sulfonamine, and *p*-methoxybenzene-sulfonamine with acetic acid, acetic anhydride and maleic anhydride. These tests confirmed the acid Lewis properties of these catalysts.

Keywords: Immobilized ionic liquid catalysts; Silica support; Acylation of sulfonamines

1. Introduction

Friedel–Crafts acylation is one of the most important reactions due to the multiple applications in organic syntheses [1]. Typically, this reaction is catalyzed by homogeneous Friedel–Crafts Lewis acid catalysts such as $AlCl_3$. However, the use of such homogeneous acid-catalysts has some major limitations including no possible reuse, air and moisture sensitivity and low product selectivity [2]. As a result one of the challenges in the field of catalysis is to replace this commonly used Lewis acid by a non-toxic, non-corrosive, easy to handle and environmentally friendly catalyst. Although heterogeneous acidic catalysts in the liquid-phase can alleviate these issues. Many of these materials, for example zeolites, often require higher reaction temperatures than those used under homogeneous conditions [3]. Also, the use of heterogeneous solid acid catalysts may lead to different selectivities than those resulted using homogeneous $AlCl_3$ [4].

Ionic liquids have been suggested as a possible replacement for Lewis acid catalysts [5]. In addition to the known properties of these compounds like negligible vapor pressure, low toxicity, stability against water, they may exhibit tunable properties due to the possibility to change both the organic cation and the inorganic anion. As well as their use as liquids, Lewis-acidic ionic liquids have been immobilized on solid supports. Hoelderich and co-workers have immobilized ionic liquids based on $FeCl_3$, $SnCl_2$, and $AlCl_3$ for Friedel–Crafts processes [6–9]. In general, the immobilization of ionic liquids on solids brings many advantages for the catalytic system, such as the easier separation from the reaction media and the possible utilization of the catalyst in a continuous system [10].

The acylation of sulfonamides has a special place among organic syntheses because of the pharmacological importance of the sulfonyl acetamides moiety [11–15]. Almost all the acylation methodologies suffer from long reaction times, stringent conditions, use of halogenated solvents or the use of

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doi:10.1016/j.cattod.2007.10.028

hazardous materials and catalysts. To avoid major environmental hazards and to satisfy growing stringent global environmental regulations, it is imperative to develop a truly catalytic process with minimal waste production.

The aim of this study was to investigate the acylation of three different sulfonamines: benzenesulfonamine (R = H), *p*-nitrobenzenesulfonamine (R = NO_2), and *p*-methoxybenzenesulfonamine (R = MeO) with acetic acid, acetic anhydride and maleic anhydride as the acylating agents using immobilized 1,3-dimethyl-3-(3-trimethoxysilylpropyl)-imidazolium tetrafluoroborate or bis{(trifluoromethyl)sulfonyl}imide ($[NTf_2]^-$) on silica supports as heterogeneous catalysts.

2. Experimental

Scheme 1 describes the preparation of immobilized ionic liquid catalysts. The ionic liquid **1** was reacted at 150 °C for 4 h under a nitrogen atmosphere with 3 chloropropyl-triethoxysilane in a molar ratio of 1:1 resulting 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium chloride (step a). This was then treated with either sodium tetrafluoroborate or lithium bis{(trifluoromethyl)sulfonyl}imide in a ratio 1:1 for 2 days in dry acetone to give the corresponding derivatives **2** and **3** (step b). Then, pretreated silica gel was refluxed with a chloroform solution of compounds **2** and **3** at 65 °C for 26 h to give, after a condensation reaction, the modified support materials.

Silica with three different textural properties were used as the supports (Table 1). Samples with small surface area and very large pore size (K1 and K2) and with a rather high surface area but with mesopores were selected (K3). These properties were determined from the adsorption–desorption isotherms of nitrogen at −196 °C using Micromeritics ASAP 2000 apparatus after outgassing the samples at 120 °C K for 24 h under vacuum. The analysis of the isotherms was made using the BET and BJH formalisms. After modifying the supports by the IL grafting process both the surface area and the average pore size of the supports diminished.

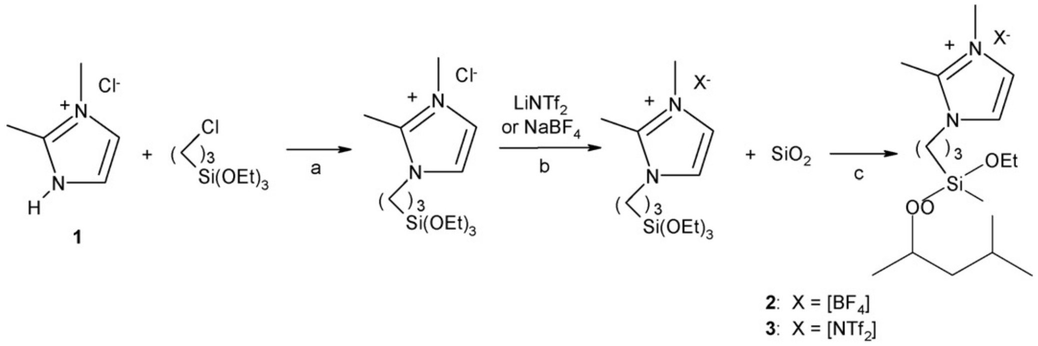
In addition to the texture, the catalysts were characterized by TG-DTA, XPS, DRIFTS, DR-UV–vis, NMR, and XRD techniques. TG-DTA measurements were performed under ambient conditions using a SETARAM 92 16.18 instrument by heating the samples to 1273 K at a rate of 10 K min^{-1}. The XRD patterns were obtained with a SIEMENS D-5000 diffractometer operated at 40 kV and 50 mA, equipped with a variable-slit diffracted-beam monochromator and scintillation counter to ensure a strict monochromatization of the X-ray beam. The diffraction patterns were recorded in the range 0–80° 2θ using Cu Kα radiation ($\lambda = 1.54183$ Å). The XPS spectra were obtained with a Leybold Heraeus spectrometer with monochromated Al Kα radiation. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ peak (binding energy: 84.0 eV). For the calculation of the binding energies, the C 1s peak of the C-(C,H) component at 284.8 eV was used as an internal standard. The composite peaks were decomposed by a fitting routine included in the ESCA 8,3 D software. The superficial composition of the investigated samples was determined using the same software. The peaks assigned to F 1s, O 1s, Si $2p_{3/2}$, N 1s, B 1s, S 2p, and C 1s levels were analyzed. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected on a Nicolet 4700 spectrometer (200 scans with a resolution of 4 cm^{-1}). Pure samples were placed inside a controlled environmental chamber attached to a diffuse reflectance accessory (Smart collector). DRIFT spectra were recorded at room temperature.

DR-UV–vis spectra were collected with a Specord250 (AnalytikJena). ^1H NMR of the analyzed ILs was performed on a 300 MHz AMX-Bürker spectrometer. TMS was used as internal standard and CD_3CN as solvent.

For the reaction, typically a mixture of sulfonamide (1 mmol), acylating agent (3 mmol) and catalyst (15 mg) in THF (4 cm^3) as solvent were stirred and reacted in a closed system at 80 °C for 18 h. At the end of the reaction, the catalyst was filtered off and the product was separated from solvent by vacuum distillation at 80 °C as a crystalline solid. The product was then re-dissolved in the HPLC eluent and analyzed. The products were characterized by HPLC-MS technique. Blank experiments carried out in the absence of any catalyst showed no conversion of the investigated substrates under the investigated experimental conditions. Recycling experiments were carried as well. The separated catalyst was reused 5 times without any pretreatment in the same experimental conditions.

3. Results and discussions

^1H NMR analysis indicated that the step "a" in the preparation procedure (Scheme 1) was successfully achieved.



Scheme 1. The preparation of SiO_2 immobilized ionic liquid catalysts.

Table 1
Textural characteristics of the investigated catalysts

Catalyst	Fresh silica		Grafted silica	
	Surface area ($m^2\ g^{-1}$)	Average pore size (nm)	Surface area ($m^2\ g^{-1}$)	Average pore size (nm)
K1	27	150	17	9
K2	40	100	10	7
K3	238	40	76	10

Table 2
Comparative TGA and calculated weight loss of the silica immobilized ILs catalysts in the range RT–600 °C

Catalyst	Weight loss from TG, %	Calculated weight loss, %
K1	41.4	39.5
K2	42.7	39.8
K3	47.5	49.1

Fig. 1 shows the ^{1}H NMR shifts confirming this aspect. Thus, the immobilization was carried out by grafting pure triethoxysilyl derivatives.

Quantitative determination of the organic content in the silicas immobilized ILs was performed by thermogravimetric analysis (TGA) in air. Table 2 shows the comparative TGA and calculated weight loss of the grafted samples. A large exothermic peak located at 370–390 °C was related to the decomposition of the organic moiety with a loss corresponding to the values indicated in Table 2. Due to the dehydroxylation of Si–OH groups a small weight loss was detected at higher temperatures. The calculated weight loss corresponds to the introduced measured amount of grafted IL. Thus, the TGA analysis shows a perfect concordance between the amount of the ionic liquid grafted on the surface and the theoretical one.

Fig. 2 shows the DRIFTS spectra of the silicas immobilized ILs. These provide good evidence of the grafting of ILs. This is shown by the almost complete disappearance of the band located at 3650 cm^{-1} corresponding to free OH groups. This result is in a perfect concordance with TGA analysis, which indicated a small concentration of surface OH groups corresponding to 4–6% compared with the pure silica, and with the measured values of the surface areas. These results are also consistent with the grafting mechanism shown in Scheme 1. In addition, these spectra contain bands located at 2965, 2946 and 2897 cm^{-1} assigned to C–H bonds, and at 1636 and 1422 cm^{-1} assigned to C–N and C–H bonds, respectively, in the investigated ILs. DR-UV–vis spectra (spectra not shown) led to the same conclusions.

Information about the integrity of these materials is also shown by the XPS data. Table 3 summarizes the XPS binding energies associated with the F 1s, O 1s, Si $2p_{3/2}$, N 1s, B 1s, S 2p and C 1s levels in the investigated catalysts. The spectra showed no evidence for the presence of chlorine demonstrating the completely replacement of the halide by tetrafluoborate and bis{(trifluoromethyl)sulfonyl}imide anions. The binding energies of the above levels are typical for these elements in the compounds we investigated [16]. Thus, for nitrogen, one component was located at 399.7 eV and assigned to imidazolium core, and another was located at 397.8 eV and assigned to bis{(trifluoromethyl)sulfonyl}imide moiety.

Table 4 compares the experimentally determined atomic ratios in the investigated catalysts with the theoretical values (F/S = 3, N/S = 1.5 (in bis{(trifluoromethyl)-sulfonyl}imide immobilized ILs), B/N = 0.5 (in tetrafluoborate immobilized ILs)). As is clearly shown the close correlation between the values confirms the integrity of the ILs grafted on the silicas. Interestingly, a comparison of the N/Si analytical ratios as determined from TG measurements (Table 2) with the XPS

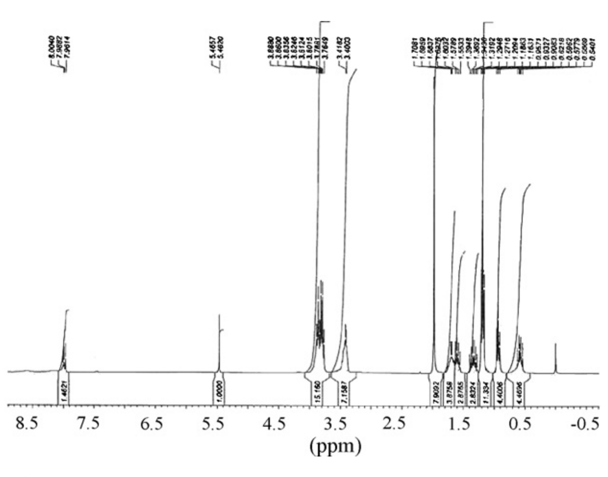


Fig. 1. ^{1}H NMR shifts of 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium chloride.

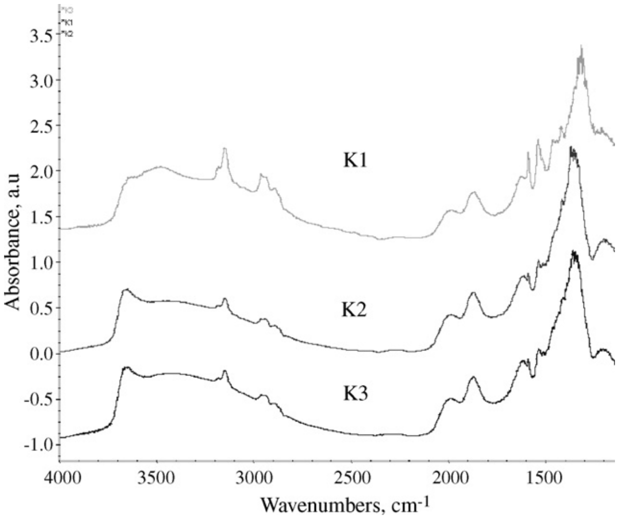
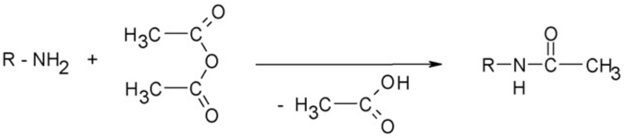
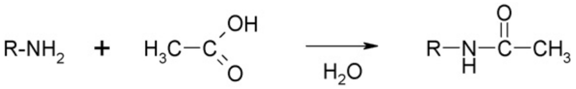


Fig. 2. DRIFTS spectra of the investigated catalysts.

Table 3
XPS binding energies (eV) of the F 1s, O 1s, Si $2p_{3/2}$, N 1s, B 1s, S 2p, and C 1s levels in the investigated catalysts

Level	IL:1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium bis{(trifluoromethyl)sulfonyl}imide	IL:1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate
F 1s	687.4	689.7
O 1s	531.6	531.6
Si $2p_{3/2}$	102.1	102.1
N 1s	399.7	399.7
N 1s	397.8	–
B 1s	–	194.7
S 2p	167.6	167.6
C 1s	291.4	291.5


Scheme 2. Acylation of the sulfonamines with acetic anhydride.


Scheme 3. Acylation of the sulfonamines with acetic acid.

determined values suggests an agglomeration of the ionic liquid on the surface of the SiO_2 support.

Fig. 3 shows the evolution of the yield to acylated compounds on these catalysts using acetic anhydride as acylating agent (Scheme 2). Several factors associated with both the substrates and the catalyst were found to influence the yield. Substituted benzenesulfonamines led to higher yields than benzenesulfonamine as well as for *p*-nitrobenzenesulfonamine compared with for *p*-methoxybenzenesulfonamine. The yield was also found to be determined by the nature of the anion and silica surface with bis{(trifluoromethyl)sulfonyl}imide ILs leading to higher yields than the corresponding tetrafluoborate salt. Moreover, the yield increased with the surface area the order was K3 > K2 > K1 which corresponds to the surface concentration of the immobilized IL as shown in Table 2.

Fig. 4 shows the results obtained using acetic acid as the acylating agent (Scheme 3). From the practical point of view the use of acetic acid is more interesting than the corresponding anhydride due to the increase in atom economy due to one molecule of acetic acid is released for each reacted molecule. However, in this case the yields in the acylated benzenesulfonamines were much smaller (bellow 10%). Similar effects of catalyst type are shown using both the acid and anhydride substrates.

Acylation of these sulfonamides with maleic anhydride (Scheme 4 and Fig. 5) showed intermediate yields which is in

Table 4
XPS atomic ratios in the investigated catalysts

XPS levels	IL:1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium bis{(trifluoromethyl)sulfonyl}imide			IL:1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate		
	K1	K2	K3	K1	K2	K3
F/S	2.96	2.94	2.97	–	–	–
N/S	1.54	1.56	1.52	–	–	–
B/N	–	–	–	0.52	0.48	0.47
S/Si	0.38	0.39	0.37	–	–	–
B/Si	–	–	–	0.20	0.21	0.18

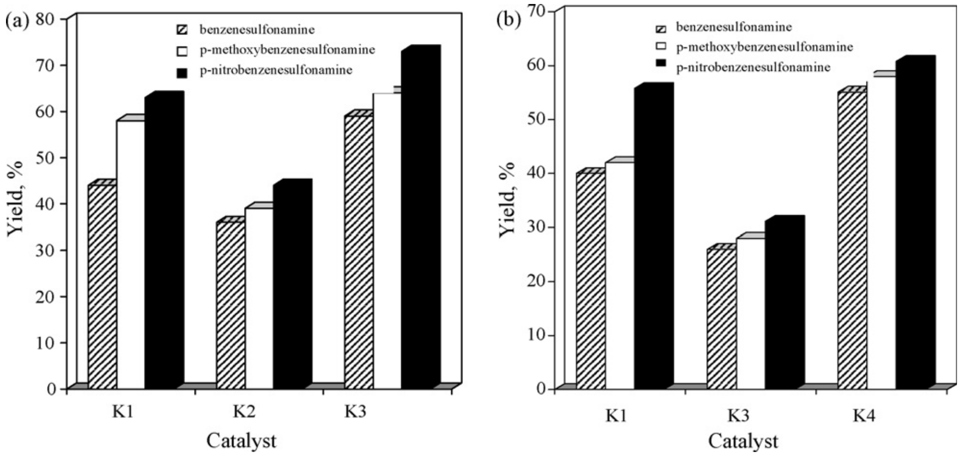


Fig. 3. The yield of acylated compounds using silica immobilized ILs based on (a) bis{(trifluoromethyl)sulfonyl}imide and (b) tetrafluoborate using acetic anhydride as acylating agent.

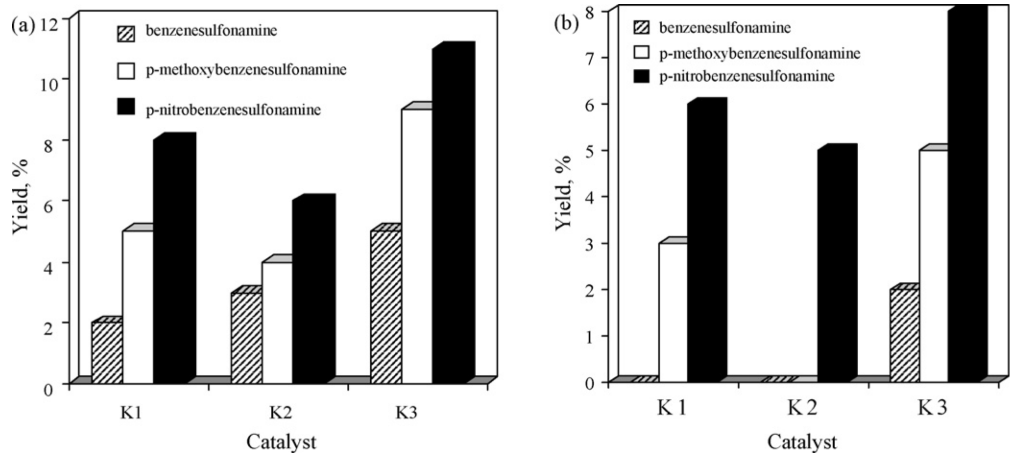


Fig. 4. The yield of acylated compounds using silica immobilized ILs based on (a) bis{(trifluoromethyl)sulfonyl}imide and (b) tetrafluoborate using acetic acid as acylating agent.

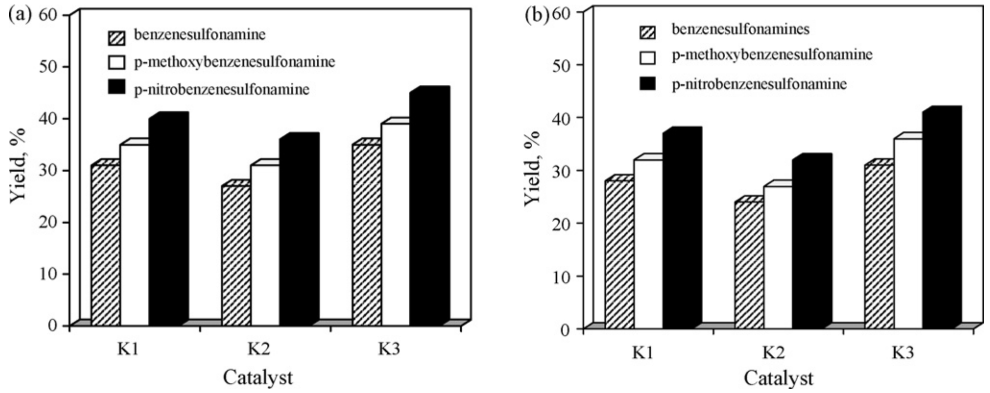
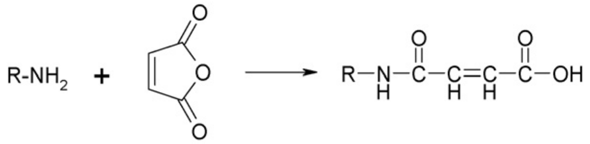


Fig. 5. The yield of acylated compounds using silica immobilized ILs based on (a) bis{(trifluoromethyl)sulfonyl}imide and (b) tetrafluoborate using maleic anhydride as acylating agent.



Scheme 4. Acylation of the sulfonamines with maleic anhydride.

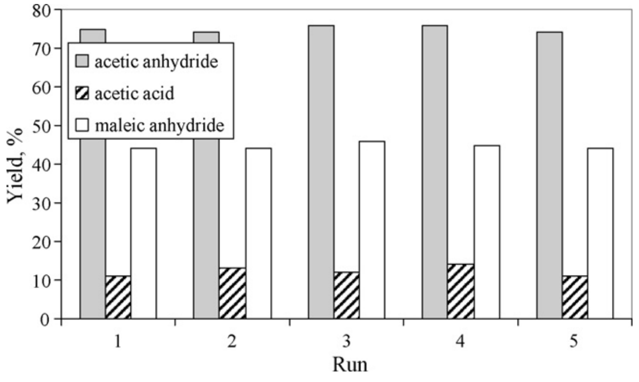


Fig. 6. Recycling experiments in acylation of *p*-nitrobenzenesulfonamine using the catalyst K3 in the form bis{(trifluoromethyl)sulfonyl}imide.

accordance with the reactivity of this agent as compared with acetic anhydride or acetic acid. The effect of the substrate and the catalyst was similar with that determined for the reactions with acetic anhydride or acetic acid.

Recycling experiments indicated these catalysts were indeed stable. Fig. 6 shows the performances of the catalyst K3 in the form bis{(trifluoromethyl)sulfonyl}imide in acylation of *p*-nitrobenzenesulfonamine using different acylating agents in five successive experiments. No real changes were evidenced during these runs.

4. Conclusions

The characterization techniques used in this study showed the success of the synthesis of immobilized ILs-Lewis acid systems onto silica surfaces via grafting of silicas with different surface areas with 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium derivatives. Testing these materials as catalysts for acylation of sulfonamines indicated they are active and stable for the synthesis of *N*-acylsulfonamines with the activity determined by the surface concentration of IL. Their use led to several advantages such as the green synthesis of acylated compounds under mild reaction conditions.

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