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Metal-triflate ionic liquid systems immobilized onto mesoporous MS41 materials as new and efficient catalysts for *N*-acylation

Simona M. Coman [a,d,*], Mihaela Florea [a,d], Vasile I. Parvulescu [a], Victor David [b],
Andrei Medvedovici [b], Dirk De Vos [c], Pierre A. Jacobs [c], George Poncelet [d], Paul Grange [d]

[a] *University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, Bdul Regina Elisabeta 4-12, Bucharest 70346, Romania*
[b] *University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Bdul Regina Elisabeta 4-12, Bucharest 70346, Romania*
[c] *Katholieke Universiteit Leuven, Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium*
[d] *Université Catholique de Louvain, Unité de Catalyse et Chimie de Matériaux Divisés, Place Croix du Sud 2/17, B-1348, Belgium*

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Abstract

Two kinds of MS41-immobilized ionic liquids (ILs) based on dihydroimidazolium and pyridinium cation were prepared using a grafting method. The second immobilization of triflate salts on these materials led to the immobilization of metal-triflate complexes into ILs. The materials thus obtained were characterized by ^{1}H NMR, XRD, N_2-sorption measurements, TG–DTA, DRIFT, XPS, TEM, and ICP-AES. The catalysts were tested in acylation of amines and sulfonamides and proved highly active and selective. For both aromatic and aliphatic amines, acylation with carboxylic acids was possible. For sulfonamides, acylation was possible only with anhydrides. Recycling the catalysts was not accompanied by any leaching of ILs or metal triflate.

Keywords: Mesoporous materials; Ionic liquids; Metal triflate; Characterization techniques; Acylation; Amines; Sulfonamides

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1. Introduction

Amides represent an important family of intermediates widely used in the synthesis of industrial chemicals, drugs, cosmetics, and food additives. The reaction is usually performed using acid anhydrides or acyl chlorides in the presence of stoichiometric amounts of amine [1,2]. On the other hand, protic and Lewis acids are well known to catalyze the acylation reaction using acetic anhydride as an acetylating agent [3–5]. But using acetic anhydride as acetylating agent and soluble bases or acids as reagents or catalysts causes important problems in the recovery of the catalyst and byproducts, leading to <50% atom economy in the consumption of acetic anhydride. Consequently, new methods to overcome the aforementioned problems are of current interest. One such method involves the use of insoluble solid acids. However, in this case the reaction rate is small, and the acetylating agent is still acetic anhydride [6]. Another solution involves metal triflates [7–12]; however, in this case, although acetic acid is used as acylating agent and the atom economy is high, the catalyst is soluble and difficult to recover from the products.

Acylation of sulfonamides also has attracted a special attention in organic syntheses because of the pharmacologic importance of the products [13–15]. As in the case of amines, most reports describe different approaches using both basic [16–18] and acidic [19,20] reaction media, with anhydrides, esters, or acyl chlorides as acylating agents. Unfortunately, the acidic catalysts are sensitive to moisture and are easily decomposed or deactivated in the presence of even a small amount of water. Furthermore, these Lewis acids cannot be recovered and reused after the reactions are completed. Replacing these acids with new water-compatible acids poses a significant challenge. Many organic transformations use rare-earth metal triflates as Lewis acid catalysts [21–23]. Because of the aforementioned disadvantages, simplification of the acylation reaction

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* Corresponding author.
E-mail addresses: s.coman@chem.unibuc.ro, simona_cmn@yahoo.com (S.M. Coman).

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through the design of new strong heterogeneous acid catalysts that can replace the conventional hazardous liquid- or traditional waste-generating Lewis-acid catalysts is very important. In this context, room temperature ionic liquids (ILs) have attracted special interest as acid catalysts in organic syntheses [24–40]. However, the use of biphasic systems requires relatively large amounts of IL, which may create some economic and toxicologic concerns, because these compounds are expensive in a potential process. Therefore, it is desirable to minimize the amount of IL used. A solution in that direction is the "immobilization" of ILs on stable, high-surface area materials. Actually, such an approach would extend the concept introduced by supported liquid phase (SLP) catalysts [41]. As in that case, immobilization aims to transfer the desired properties (inclusively catalytic) of the ILs to a solid catalyst.

Several examples of immobilized IL-based catalysts have been reported in the literature [42–52]. Compared with other well-known acid catalysts (e.g., silica-alumina, zeolites), immobilized ILs have several advantages. The most important of these may be the easily tunable acidity, but the possibilities presented by the choice of the support material and its properties (e.g., surface area and pore width) should not be neglected. Furthermore, changing the length of side chains of the organic cation can enhance the hydrophilicity or hydrophobicity of the surface. Compared with pure ILs, immobilized ILs offer additional features; they facilitate the catalyst recovery and can be used in gas-phase reactions.

To avoid the aforementioned problems, the present work combines the properties of ILs and metal triflates and proposes new catalysts in which complex metal triflate–IL systems are immobilized onto MS41 mesoporous supports using a grafting method. They provide green, stable, recyclable heterogeneous catalysts for the acylation of amines (with acetic acid) and sulfonamides (with acetic anhydride) under green conditions and with very high atom economy. The synthesis of these green catalysts and their characterization confirming the immobilization is described.

2. Experimental

2.1. Catalyst preparation

The MCM-41 support was prepared following the well-reported procedure using cetyltrimethylammoniumchloride (CTMACl) as a structure-directing agent [53]. The Si:TEAOH (tetraethylammoniumhydroxide):CTMACl:H_2O molar composition of the gel was 1.00:0.223:1.17:29.125. To 19.27 g of LUDOX AS-40 (DuPont, 40 wt% colloidal silica in water) were added 19.43 g of tetraethylammoniumhydroxide (TEAOH) (20% in water) and 16.16 g of cetyltrimethylammoniumchloride (CTMACl). The resulting gel was kept for 15 min under stirring, after which another 32.33 g of CTMACl was added. The white precipitate was parted in two Teflon-lined autoclaves and allowed to age for 24 h at 383 K. The solid was filtered under vacuum, thoroughly washed with water and hot ethanol, and dried for 24 h at 333 K. The structure-directing agent (CTMACl) was completely removed by calcination in air at 813 K (heating rate, 1 K/min) for 10 h.

The grafting of 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate was done in several steps:

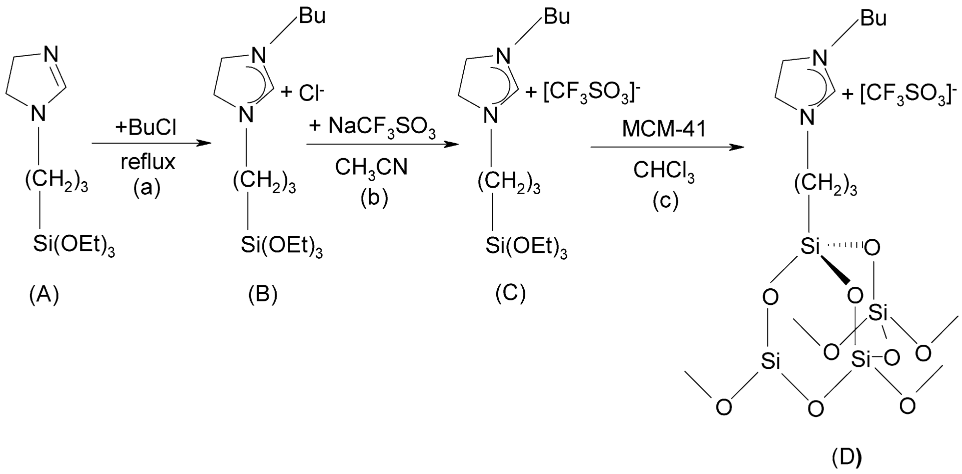
Step (a) To 0.05 mol of *N*-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazole (A), 0.15 mol of chlorobutane was added dropwise, at room temperature, under stirring and nitrogen atmosphere. The mixture was then refluxed at 348 K for 21 h. Then the volatiles were evaporated under vacuum to remove any unreacted chlorobutane and imidazole compound. The resulting 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (B) was first washed with pentane and dried under vacuum, and then extracted in dichloromethane and filtered through a bed of active carbon and alumina (previously dried at 423 K under vacuum). The residual volatile compounds were removed under reduced pressure (30 mbar) at 353 K.

Step (b) The 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride compound (0.016 mol) was dissolved in acetonitrile and stirred with 1 equivalent of NaOTf for 4 days under nitrogen atmosphere, at room temperature. Then the light-yellow slurry was filtered through a bed of Celite to remove the precipitate. After the evaporation of the volatile compounds under reduced pressure at 353 K, the product was extracted in dichloromethane and filtered through a bed of active carbon and alumina. Finally, the volatile compounds were removed under reduced pressure at 353 K. The resulting product was the IL 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate (C).

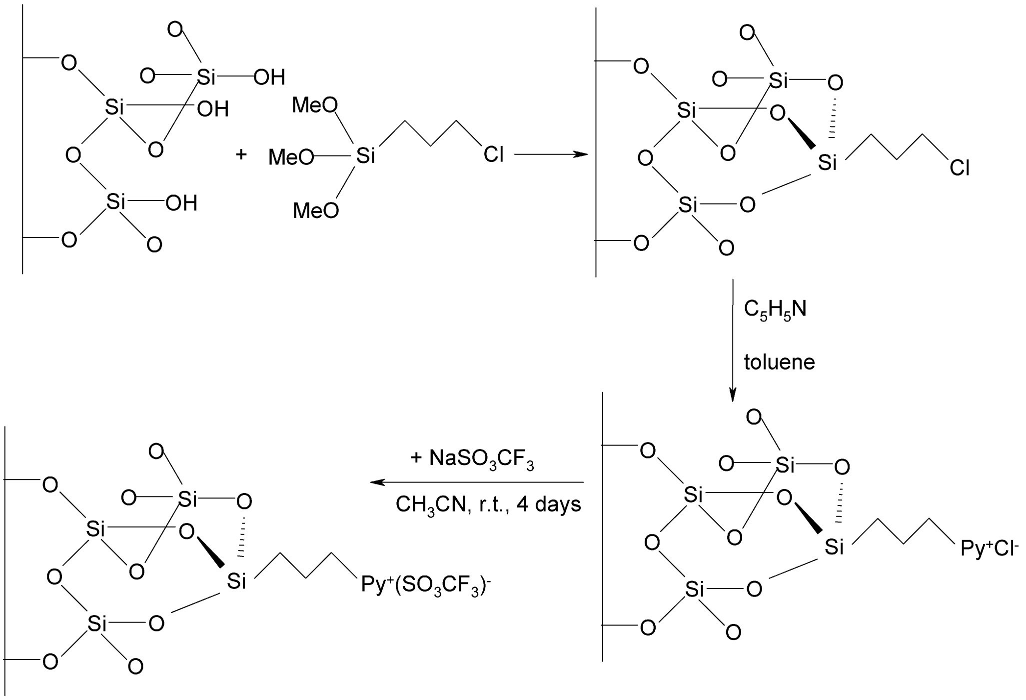
The results of ^1H NMR done on the unsupported IL, 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate, are in agreement with the ^1H NMR results of Afeworki et al. [47] obtained for 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium tetrafluoroborate, demonstrating that the synthesis of the triflate IL was successful: ^1H NMR (300 MHz): 0.59 (m, 2H, –$\mathit{CH_2}$–CH_2–Si); 0.93 (tr, 3H, $J = 8.1$ Hz, CH_2–CH_2–$\mathit{CH_3}$, *n*-butyl); 1.20 (tr, 9H, $J = 7.6$ Hz, $\mathit{CH_3}$–CH_2–O–Si); 1.34 (m, 2H, CH_2–$\mathit{CH_2}$–CH_3, *n*-butyl); 1.60 (m, 2H, $\mathit{CH_2}$–CH_2–CH_3, *n*-butyl), 1.70 (m, 2H, CH_2–$\mathit{CH_2}$–Si); 3.41 (m, 4H, Si–CH_2–CH_2–$\mathit{CH_2}$–N; N–CH_2–$\mathit{CH_2}$–N–Bu); 3.80 (m, 6H, CH_3–$\mathit{CH_2}$–O); 3.88 (m, 4H, N–$\mathit{CH_2}$–CH_2–CH_2–CH_3; N–$\mathit{CH_2}$–CH_2–N–Bu); 7.98 (s, 1H, N–CH–N) ppm.

Step (c) First, 1.6 mmol of IL (C) was reacted with 1 g of MCM-41 support in 100 mL of chloroform at reflux conditions under stirring for 24 h. The unreacted molecular species were removed by successive washings of the solid material with pentane, acetonitrile, and diethyl ether. The separated solid was finally dried under vacuum (30 mbar) at 373 K overnight, resulting in IL-MCM [(D) in Scheme 1].

Step (d) IL-MCM (0.804 mmol IL) was mixed with 1 mmol of $Zn(SO_3CF_3)_2$ dissolved in 100 mL of acetonitrile, and stirred at room temperature for 21 h. The solid thus obtained was separated by filtration and washed with large amounts of acetonitrile to remove weakly bound species. The solid was dried first at



Scheme 1. Grafting of the imidazolium based ionic liquid onto MCM-41 support (IL-MCM sample).



Scheme 2. Grafting of the pyridinium based ionic liquid onto MCM-41 support (OTf-MCM sample).

room temperature and then at 373 K overnight. The resulting sample was designated ZnIL-MCM.

A similar procedure was followed for the preparation and immobilization of scandium triflate in supported 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate. This sample was designated ScIL-MCM.

2.1.1. Grafting of the (3-chloropropyl)trimethoxysilane

First, 1.6 mmol of (3-chloropropyl) trimethoxysilane was dissolved in 100 mL of chloroform, and 1 g of MCM-41 was added. The slurry was heated under reflux for 24 h and then cooled to room temperature, at which point the solid was separated by filtration; washed with 50 mL of pentane, 100 mL of acetonitrile, and 100 mL of diethyl ether; and dried under vacuum, resulting in the intermediate Cl-MCM (see Scheme 2). The chloropropylated solid was then treated with an excess of pyridine (2 g of pyridine for every 1 g of chloropropylated solid) and heated under reflux for 24 h. Then the slurry was cooled to room temperature, at which point the solid was separated by filtration, washed with 100 mL of toluene, and finally dried under ambient conditions. The solid was then treated with 1 equivalent of NaOTf, and the mixture was stirred at room temperature under nitrogen atmosphere for 4 days. The solid was filtered, washed with methanol, and dried under reduced pressure (30 mbar). The resulting sample was designated OTf-MCM.

Scandium triflate and zinc triflate were anchored on OTf-MCM by treating it with 1 mmol of $Sc(SO_3CF_3)_3$ [or $Zn(SO_3CF_3)_2$] dissolved in 100 mL of acetonitrile and stirred at room temperature for 21 h. After reaction, the catalyst was separated by filtration and washed with large amounts of acetonitrile to remove weakly bounded species. The solid sample was then dried at room temperature and at 373 K overnight. These samples were designated ScOTf-MCM and ZnOTf-MCM.

For comparison, the MCM-41 materials impregnated with scandium and zinc triflate were also tested. The impregnation procedure was similar to those used for the impregnation of the IL-MCM and OTf-MCM samples with triflate species. The resulted samples were designated Sc-MCM and Zn-MCM, respectively. Furthermore, to check whether the porosity of the support had any influence on the catalytic performance, silica also was impregnated with the same amounts of triflates. The samples thus obtained were designated Sc-SiO_2 and Zn-SiO_2.

2.2. Catalyst characterization

^{1}H nuclear magnetic resonance of 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate Routine analysis was performed on a 300-MHz AMX-Bruker spectrometer, with TMS as the internal standard and CD_3CN as the solvent.

X-ray diffraction XRD patterns were recorded with a Siemens D5000 Matic diffractometer equipped with a Cu$K\alpha$ radiation source. The diffractograms were recorded between 1° and 35° 2θ at a scanning speed of $1^\circ(2\theta)/\text{min}$.

N_2 sorption measurements Adsorption and desorption isotherms of N_2 at 77 K were recorded with a Micromeritics ASAP 2010 device. Before measurement, the samples were outgassed overnight at 373 K under vacuum.

Diffuse reflectance infrared Fourier transform spectroscopy DRIFTS spectra were collected with a Bruker IFS88 spectrometer (200 scans with a resolution of 4 cm^{-1}). Pure samples were placed inside a commercial controlled environment chamber (Spectra-Tech 0030-103) attached to a diffuse reflectance accessory (Spectra-Tech collector).

XPS spectroscopy XPS spectra were recorded using a SSI X-probe FISONS spectrometer (SSX-100/206) with monochromated Al$K\alpha$ radiation. The spectrometer energy scale was calibrated using the $Au_{4f_{7/2}}$ peak. For calculation of the binding energies, the C_{1s} peak of the C–(C, H) component at 284.5 eV was used as an internal standard. The peaks assigned to the F_{1s}, O_{1s}, N_{1s}, C_{1s}, S_{2p}, and Si_{2p} levels were quantitatively analyzed.

TG–DTA TGA curves were recorded with a SETARAM TGA 92 device (293–1.273 K, 2.5 K/min, 50 mL/min of air).

Transmission electron microscopy Transmission electron microscopy (TEM) measurements were performed by placing the materials on a special structured 4-nm-thick carbon support film. (These thin films are sufficiently stable to cover copper grids with a mesh of 60 µm without an additional holey organic film.) The electron microscopy investigation was carried out on a Siemens Elmiskop 102 instrument.

Elemental analyses were performed by atomic emission spectroscopy with inductively coupled plasma atomization (ICP-AES).

2.3. Catalytic tests

Acylation of amines The acylation reactions were carried out under solvent-free conditions in a closed system (glass vials with stirring) at amine: acylating agent molar ratio of 1:10. Different amines were used as substrates, including *n*-butylamine, 1-pentylamine, hexylamine, *N*-methyl-cyclohexylamine, aniline, and 2-ethylaniline. Acetic, propionic, and *n*-butyric acids were used as acylating agents. The reaction temperatures were room temperature and 80 °C. After the reaction was stopped, the catalyst was filtered and the product separated. The product was then analyzed by GC–MS.

Acylation of sulfonamides In a typical procedure, a mixture of sulfonamide (1.25 mmol), acylating agent (3.75 mmol), and catalyst (15 mg) in THF or acetonitrile (4 mL) as the solvent, was stirred at 80 °C for 18 h. Different sulfonamides were used as substrates: benzenesulfonamide, 4-nitrobenzenesulfonamide, 4-methoxybenzenesulfonamide, and *N*-phenylmethanesulfonamide. Acetic acid and acetic anhydride were used as acylating agents. After the reaction was stopped, the catalyst was filtered and the product separated from the solvent by vacuum distillation at 80 °C. The resulting product, a crystalline solid, was then redissolved in the HPLC eluent and analyzed. The products were characterized by HPLC–MS.

2.4. Analysis of the reaction products

Amine acylation products The analytical system used to follow the changes in the concentrations of the components in the reaction mixture comprised a Hewlett Packard 5880A gas chromatograph equipped with an HP 7673A automatic sample injector, a flame ionization detector (FID), and a capillary column (50 m long, 0.32 mm i.d., 1.20 µm film thickness). The reaction products were identified using a MD 800 mass spectrometer from Fisons Instruments (EI^+-ionization at 70 eV, mass max. 500–600) coupled to a gas chromatograph with a Chrompack CP-SIL 5CB column.

Sulfonamide acylation products HPLC–MS measurements were performed with an Agilent 1100 liquid chromatograph composed of a degasser, quaternary pump, thermostated autosampler, column thermostat, atmospheric pressure chemical ionization interface (APCI), ion trap mass spectrometric detector (SL series), and nitrogen generator.

Chromatographic conditions A monolithic Chromolith Performance RP-18e (Merck, Germany; 100 mm long, 4.6 mm i.d.) was used. The column was thermostatted at 40 °C. Elution was isocratic with a flow rate of 0.8 mL/min, using a mobile phase comprising 35% methanol and 65% of 0.1% formic acid solution.

Interface parameters The parameters controlling the APCI interface were as follows: drying gas flow, 10 L/min; drying gas temperature, 350 °C; pressure of the nebulizer gas pressure, 60 psi; capillary voltage, 4500 V; and high-voltage end plate offset, −500 V. All solvents used were HPLC grade from Merck KGaA (Darmstadt, Germany).

3. Results and discussion

As shown in Section 2, ^{1}H NMR analysis of the 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate demonstrated successful synthesis of the triflate IL. Powder XRD patterns of IL-MCM and OTf-MCM, presented in Fig. 1, exhibit only the diffraction lines of the MS41 structure, namely mesoporous materials with two-dimensional hexagonal symmetry (honeycomb structure), providing good evidence that the structure of the mesoporous materials was preserved throughout all of the treatments to which these materials were exposed (i.e., tethering, extraction of the structure directing agent).

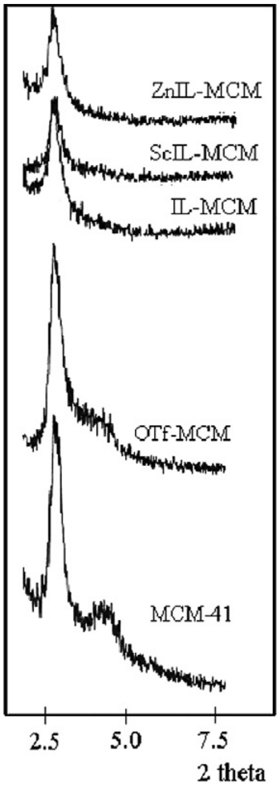


Fig. 1. XRD diffractograms for IL-MCM, ScIL-MCM, ZnIL-MCM and OTf-MCM samples.

Table 1
Surface area and mesoporous volume of some catalytic samples

Sample	S_{BET} (m^2/g)	$V_{p\ meso}$ (cm^3/g)	Pore diameter (nm) (BJH method)
MCM-41	544	0.195	2.7
IL-MCM	90	0.030	2.2(+3.5)
OTf-MCM	304	0.110	2.7(+4.2)
ScOTf-MCM	258	0.090	2.7(+4.2)

The tethering of IL induced some slight differences in the XRD patterns, however. The pattern of the OTf-MCM sample contained the dominant d_{100} reflection, but with the long-range order lines merged together into a broad peak. The lower intensity of the d_{100} peak compared with MCM-41 is characteristic of all grafted organo-ordered silicas. Treatment with Sc(OTf)$_3$ or Zn(OTf)$_2$ was not accompanied by any characteristic line of the metallic compound, indicating that indeed the final material contained only dispersed docked species. These samples correspond to the textural characteristics of the hybrid materials presented in Table 1.

Nitrogen adsorption–desorption isotherms of the materials showed typical type IV shapes as generally reported for mesoporous materials. However, as for the XRD patterns, differences among these were observed. These correspond to the values presented in Table 1. The variation of the surface areas ran parallel with the intensity of the d_{100} line observed in the XRD patterns. Thus, for sample IL-MCM, a drastic reduction in the surface area was observed compared with the parent MCM-41. This drop may be related to the blocking of the pores by 1-butyl-3-(3′-triethoxysilylpropyl)-4,5-dihydroimidazolium triflate IL (which penetrated inside).

The volume developed by the mesopores and the pore diameter decreased in the same way as the surface area. Even so, after grafting of the IL, the textural characterization indicated that larger mesopores also were created. A reduction in pore size also occurred. Moreover, during the grafting process, a fraction of IL may have become attached to the external surface of MCM-41 and part of the mesopores may have been destroyed in this process, leading to the formation of macropores.

TEM images of the materials confirmed the mesoporous structure even after grafting of the organic functionality (Figs. 2a and 2b).

DRIFTS analysis of IL-MCM confirmed that the grafting of IL resulted in functionalized materials with intact organic groups. Table 2 summarizes all of the bands identified for MCM-41 and IL-MCM-41.

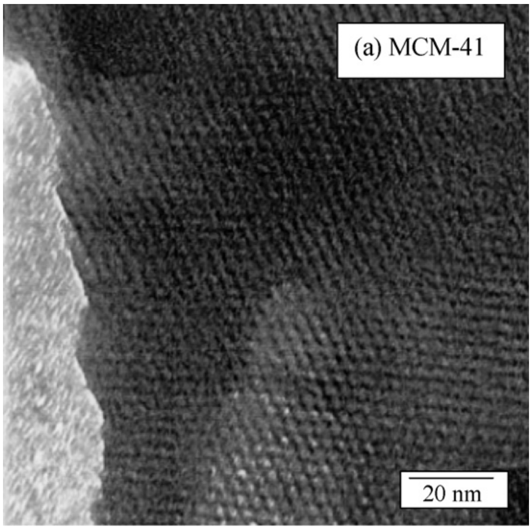
Fig. 3 shows the change in the Si–OH stretching band at 3745 cm^{-1} before and after docking of the ILs. The disappearance of this band, accompanied by the appearance of all of the characteristic bands of IL, constitutes strong evidence for the nondestructive tethering of these substrates. Moreover, this disappearance indicates full coverage of the MCM support with the IL.

Table 3 presents the binding energies (in eV) of the main elements of the IL-MCM-41 catalyst, along with the atomic XPS and chemical F/S, N/S, S/Si, and N/Si ratios. Unfortunately, the 2p$_1$ binding energy of Sc is superimposed with the 1s signal of N, and the deconvolution of the peaks does not provide accurate results.

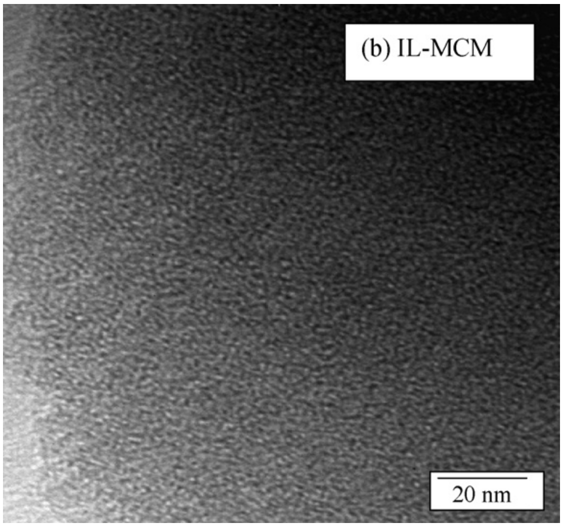
It is already known that the physical and chemical properties of ILs can be altered by the presence of impurities arising from their preparation. Thus, purification of the IL is essential. The main contaminants are halide anions or organic bases that generally come from unreacted starting material. The halide impurities can have a detrimental effect on transition metal-

Table 2
Frequency and group assignments for the IL-MCM sample

Wavenumber (cm^{-1})	Group assignment		Comment
	MCM-41	IL-MCM-41	
3745 (s)	Free silanol hydroxyl band, str.	–	Si–OH stretching (sharp band)
3730–3500 (s)	Bridged silanols, str.	Bridged silanols, str.	Si–OH groups with strong hydrogen-bonding interaction (broad band)
3500–3400	H_2O –SiOH	H_2O–SiOH	Molecular adsorbed water
2969 (m)	–	$–OCH_2–$, asym. str.	C–H asymmetric stretching
2937–2882 (m)	–	$–CH_2–$ str. (asym. and sym.)	C–H (a)symmetric stretching
1873 (w)	–Si–O–, str.	–Si–O–, str.	Stretching, combination band
1662 (s)	–	–C=N, str.	
1632 (m)	–OH (H_2O)	–OH (H_2O)	Bending OH, molecular water
1530	–	SO_3CF_3	
1451	–	$–OCH_2–$, str.	Asymmetric bending
1250–1000	–Si–O–Si–	–Si–O–Si– and Si–C	Asymmetric stretching mode



(a)



(b)

Fig. 2. TEM microscopy of the MCM-41 (a) and IL-MCM (b) samples.

catalyzed reactions. With respect to this, it is very important to note that the XPS spectra of the supported ILs showed no peak that can be associated with the binding energy of chlorine. This result also demonstrates that all of the IL was covalently bonded and that no residual IL remained. The comparison of the N/Si analytical ratio with the N/Si XPS ratio is consistent with an agglomeration of the IL on the surface of the mesoporous support (see Table 3), which is in complete agreement with expectation and with the XRD and N_2 sorption measurements. The F/S ratio of 2.61–2.84, as determined by XPS, also confirms the preservation of the triflate structure (the theoretical F/S ratio in the triflate structure is 3) in IL-supported samples designated as IL-MCM and OTf-MCM.

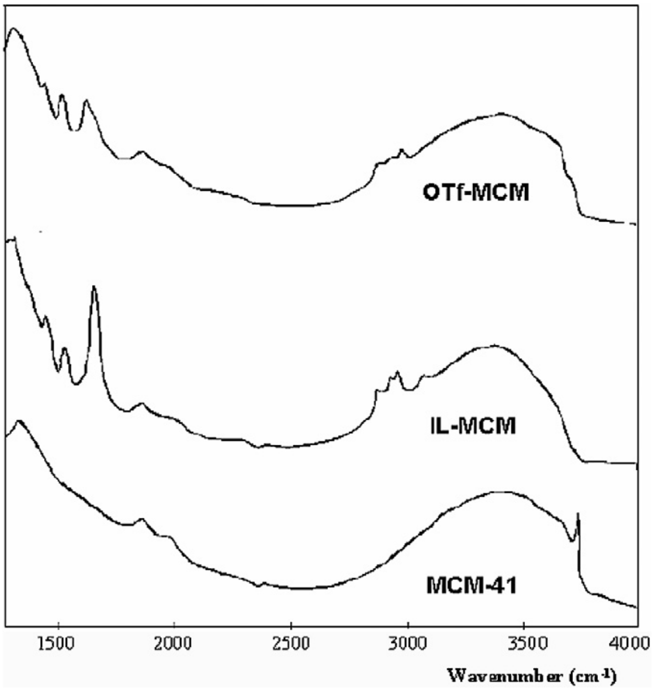


Fig. 3. DRIFT spectra of MCM-41, IL-MCM-41, and OTf-MCM samples.

The triflate anion also could be docked directly to MCM via ionic interactions with the surface hydroxyl groups, generating species as in Scheme 3 [54]. Such a direct interaction of the triflate salt with the support surface determines the increase of the S/Si XPS ratio (Table 3, entry 10). On the other hand, the absence of hydroxyl groups after grafting of the IL makes such interactions impossible. Therefore, the increased S/Si XPS ratio is merely an indication of the presence of the triflate salt in the final catalyst, which can be immersed into the grafted IL.

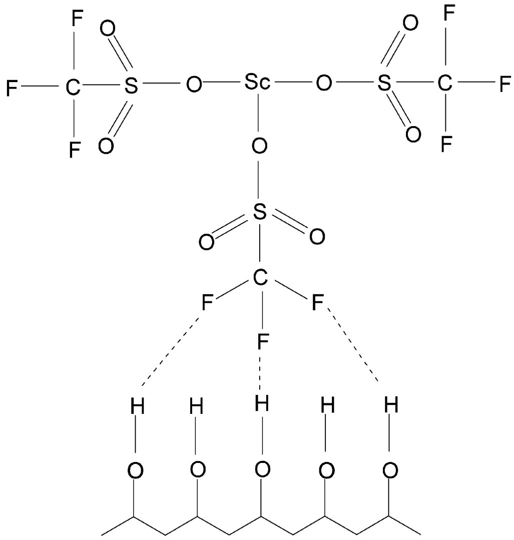
Moreover, the analytical analysis (ICP-AES) of Sc and Zn indicated good concordance with the theoretical values. Indeed, the concentration of these two elements established by ICP-AES was 3.3 wt% for Sc and 5.1 wt% for Zn, whereas the theoretical amount corresponding to the metal content in ILs was 4.0 wt% for Sc and 6.5 wt% for Zn.

Quantitative determination of the organic content in the hybrid mesoporous silicas was done by thermogravimetric analysis (TGA) in air. Fig. 4 shows the weight loss curves of the grafted samples. The large exothermic peak at 370–380 °C is related to decomposition of the organic moiety, with losses of 45.6 wt% for IL-MCM and 59.4 wt% for ScIL-MCM (Fig. 4). The theoretical amounts of the organic moiety were 43.5 wt% for IL-MCM and 50.4 wt% for ScIL-MCM. Due to the dehydroxylation of the Si–OH groups, a small weight loss was detected at higher temperatures. Thus, the TGA analysis shows perfect concordance between the amount of the IL grafted on the surface and the theoretical amount.

Table 3
Binding energies (eV) of the main elements of the IL-MCM, ScIL-MAM, ZnIL-MCM and OTf-MCM catalysts, and XPS and calculated N/Si ratio

Element	B.E. (eV)			
	IL-MCM-41	ScIL-MCM-41	ZnIL-MCM-41	OTf-MCM-41
Zn_{2p}	–	–	1020.6	–
F_{1s}	687.4	686.9	686.8	687.4
O_{1s}	531.5	531.3	531.0	531.4
N_{1s}	399.7	399.7	399.2	399.6
C_{1s}	291.4	291.2	291.9	291.3
S_{2p}	167.6	167.6	167.3	167.7
Si_{2p}	102.4	102.2	102.8	102.4
F/S	2.84	2.64	2.61	2.89
N/S	1.85	0.75	0.66	0.89
S/Si	0.15	0.45	0.41	0.16

Note. N/Si (XPS) = 0.278; N/Si (calc.) = 0.070.



Scheme 3. Possible docking of scandium triflate onto MCM-41 surface via ionic interactions with the surface hydroxyl groups.

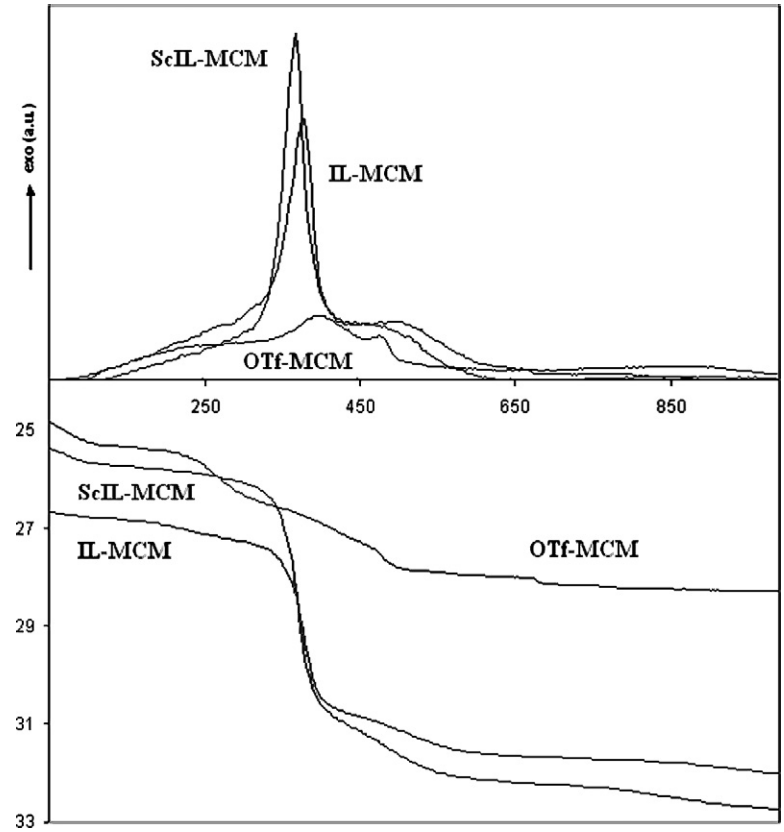


Fig. 4. TGA and DTA curves for ILs grafted onto the surface of the MCM-41 support (IL-MCM: weight loss—45.63%, theoretical—43.46%; ScIL-MCM: weight loss—59.39%, theoretical—50.97%; OTf-MCM: weight loss—37.72%, theoretical—36.62%).

Scheme 4 gives a picture of the prepared catalysts based on the results of the characterization techniques.

Table 4 reports the results obtained in the acylation of aniline with acetic and propionic acid in the presence of Zn-MCM, Sc-MCM, Zn-SiO_2, and Sc-SiO_2 at room temperature. Under these conditions and with these catalysts, the reaction rate was quite low; after 23 h, the conversion of aniline was <25%. In addition, selectivity to the amide was not satisfactory, <90% in all cases. The data obtained from these reactions gives information about the influence of the nature of the support as well. Therefore, as Table 4 shows, higher conversions are obtained for the silica-based catalysts than for the MCM-based samples. The increased conversions obtained for the silica-based catalysts should be coupled with lower selectivities than those obtained with MCM-based samples. These results clearly show that the nature of the support is also important in such reactions.

Heating the mixture at 80 °C led to an important increase of the reaction rate; under these conditions, the reaction with butyric acid was also possible. Of note, the increased activity was accompanied by an increase in selectivity, with only the amide detected (Table 5).

Table 4
The acylation of aniline in the presence of MCM-41 and SiO_2 impregnated with scandium and zinc triflates (RT, aniline/acylating agent molar ratio of 1/10, 23 h)

Entry	Catalyst	Acylating agent	Conversion (%)	Selectivity to amide (%)
1	Zn-MCM	Acetic acid	17.2	87.8
2	Sc-MCM		21.2	67.0
3	Zn-SiO_2		22.3	51.6
4	Sc-SiO_2		24.6	50.1
5	Zn-MCM	Propionic acid	14.7	73.8
6	Sc-MCM		11.2	21.1
7	Zn-SiO_2		18.3	60.1
8	Sc-SiO_2		14.9	15.2

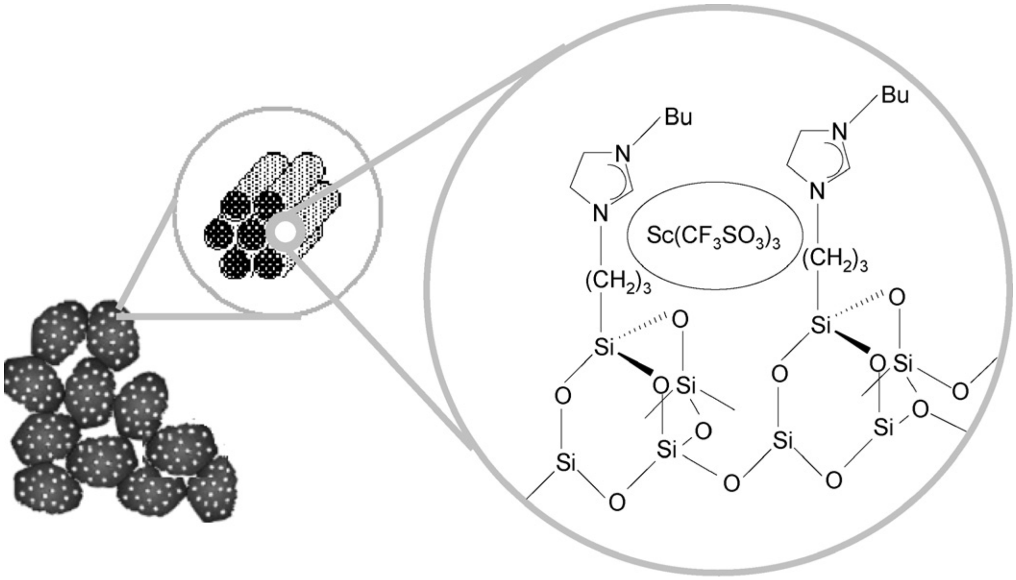
The IL-MCM and OTf-MCM catalysts were slightly more active than the Zn-MCM or Sc-MCM catalysts. No synergistic effect between metal triflate and IL was observed in this case. Practically, these results provide no evidence of the contribution of metal triflate in these reactions. The acylation of aniline in the presence of immobilized IL led to high selectivity, reaching 100% in the presence of acetic acid, irrespective of the catalysts.

Comparing the results of MCM-immobilized triflates salts [e.g., Sc-MCM or Zn-MCM (entries 1, 2, 7, 8, 13, and 14 in Table 5)] and IL-MCM-immobilized triflate salts [e.g., ScIL-MCM and ZnIL-MCM samples (entries 4, 5, 10, 11, 16, and 17 in Table 5)] shows that after 21 h, higher selectivities were ob-

Table 5
Conversion of aniline in the presence of triflate salts-MCM and ionic liquids based catalysts (aniline/acylating agent = 1/10, 21 h, 80 °C)

Entry	Catalyst	Acylating agent	Conversion (%)	Selectivity to amide (%)
1	Sc-MCM	Acetic acid	79.5(100)[a]	100
2	Zn-MCM		79.2(90.2)[a]	100
3	IL-MCM		85.8(97.6)[a]	100
4	ScIL-MCM		83.3(96.0)[a]	100
5	ZnIL-MCM		84.2(96.0)[a]	100
6	OTf-MCM		82.1(92.3)[a]	100
7	Sc-MCM	Propionic acid	73.5	85.8
8	Zn-MCM		72.9	81.3
9	IL-MCM		79.2	88.2
10	ScIL-MCM		77.5	90.6
11	ZnIL-MCM		78.0	92.4
12	OTf-MCM		78.7	94.2
13	Sc-MCM	Butyric acid	54.7	92.3
14	Zn-MCM		53.2	91.6
15	IL-MCM		58.4	93.7
16	ScIL-MCM		59.8	95.0
17	ZnIL-MCM		57.4	96.1
18	OTf-MCM		55.2	95.1

[a] Conversion (%) after 40 h.

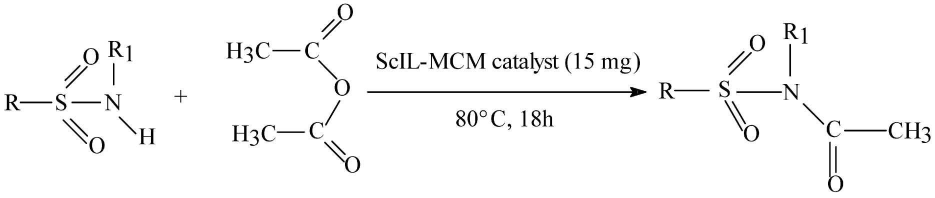


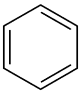
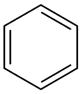
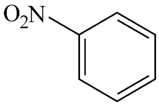
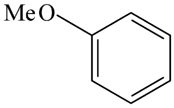
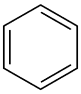
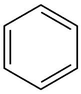
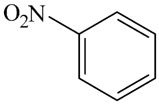
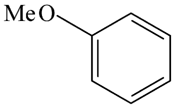
Scheme 4. Ideal picture of the catalyst based on the results of the characterization techniques.

Table 6
Acylation of different kinds of amines in the presence of acetic acid (amine/acetic acid = 1/10, 80 °C, 24 h)

Amine	Sc-MCM		IL-MCM		ScIL-MCM	
	C (%)	S (%)	C (%)	S (%)	C (%)	S (%)
n-Butylamine	4.24	83.02	18.3	93.58	100	95.22
n-Pentylamine	5.52	85.14	6.63	83.19	100	96.32
n-Hexylamine	4.86	97.72	6.66	89.74	100	98.18
2-Ethylaniline	37.66	97.89	41.35	100	45.79	100
N-methyl-cyclohexyl-amine	22.03	85.88	20.25	95.60	97.32	95.94

Table 7
Acylation of sulfonamides



Entry	R	R_1	Solvent	TOF (h^{-1})[a]	Yield (%)
1		H	CH_3CN	161.4	85.0
2	CH_3–		CH_3CN	65.4	68.7
3		H	CH_3CN	147.6	77.6
4		H	CH_3CN	159.7	73.3
5		H	THF	82.8	43.4
6	CH_3–		THF	61.3	32.2
7		H	THF	79.0	41.5
8		H	THF	74.4	39.1

[a] mmol of transformed substrate/(mmol of active phase × time).

tained with IL-MCM-immobilized triflate salts. As mentioned above, the reaction was also done with propionic and *n*-butyric acids as acylation agents, resulting in satisfactory conversions and selectivities (e.g., for propionic acid, a conversion of 90–95% reached after 50 h).

Table 6 gives the results collected for the same catalysts in the acylation of different acyclic and cyclic amines with acetic acid. The results demonstrate that conversion depended on the length of the aliphatic chain. However, for the acylation of these substrates, a synergistic effect of the presence of IL and metal triflates was found. Indeed, the conversion was improved from several percent on Sc-MCM and IL-MCM to 100% on ScIL-MCM. The best selectivities to *N*-monoacylamine were obtained in the presence of ScIL-MCM. The decreased selectivity to *N*-monoacylamine amide is due to formation of the *N*,*N*-diacylamines.

For the acylation of sulfonamide, an initial screening was conducted at 80 °C using combinations of two solvents (CH$_3$-

CN and THF), two acylating agents (acetic anhydride and acetic acid), and six catalysts. Under these conditions, no acylation of sulfonamide with acetic acid was observed. Using acetic anhydride as the acylating agent, the best results were obtained using ScIL-MCM in CH_3CN. These results can be attributed to the solvent's ability to stabilize the acylium intermediate. To provide a general method of access into the acylated sulfonamides, this method was applied to a set of sterically and electronically diverse sulfonamides. As shown in Table 7, the reaction gave generally high yields and worked on most of the substrates tested. Generally, the electronic nature of the sulfonamide had little effect on the efficiency of the process, whereas the steric bulk had a greater influence.

Generally, in the presence of a Lewis acid, the acylating agent forms adducts via the carbonyl oxygen atoms. As a result, the carbonyl bond is strongly polarized, and the carbon atom becomes sufficiently electrophilic to interact with the substrate to allow the reaction to occur. From this standpoint, the carboxylic acids are more stable than acidic chlorides and carboxylic anhydrides, and thus they are less reactive. Two options are available for activating these acylating agents: using a high reaction temperature or using a catalyst of strong acidity (even superacidity). The immobilized IL catalysts, alone or in combination with metal triflates, are able to acylate both aromatic and aliphatic amines directly with carboxylic acid, which is indeed remarkable. Acylation of the sulfonamides did not occur with carboxylic acids, mainly because of an advanced interaction of these molecules with the catalysts.

4. Conclusion

Immobilization of IL and IL–metal triflate catalysts onto mesoporous MCM-41 surface was successfully achieved and confirmed by several characterization techniques: ^1H NMR chemical shifts, DRIFTS, XPS, N_2 sorption measurements, TGA, and chemical analysis. Green catalysts were synthesized following the preparation procedures described herein.

The resulting materials proved to be efficient catalysts for the acylation of amines under green conditions and with a very high atom economy by directly using acetic, propionic, and butyric acids as acylating agents instead of acid anhydride. The reactions were carried out under mild reaction conditions. These materials are also suitable catalysts for the synthesis of *N*-acylsulfonamides from sterically and electronically diverse aromatic substrates, but in that case, acylation was possible only with acetic anhydride.

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Supplementary material

The online version of this article contains additional supplementary material.

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