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Supported ionic liquids: ordered mesoporous silicas containing covalently linked ionic species

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Ordered mesoporous silicas with hexagonal or lamellar architectures incorporating covalently bound ionic species were synthesized *via* a template directed hydrolysis–polycondensation of tetraethoxysilane (TEOS) with triethoxysilylated imidazole [$(EtO)_3Si(CH_2)_3$–Im] or alkylimidazolium halides [$(EtO)_3Si(CH_2)_3$–Im^+–R Hal^-].

In recent years, room temperature ionic liquids (RTILs) have attracted growing interest as potential replacement media for volatile organic solvents in organic synthesis and catalysis.[1] As both the anionic and the cationic part of RTILs can easily be varied, the properties of these compounds can be tuned for specific purposes.

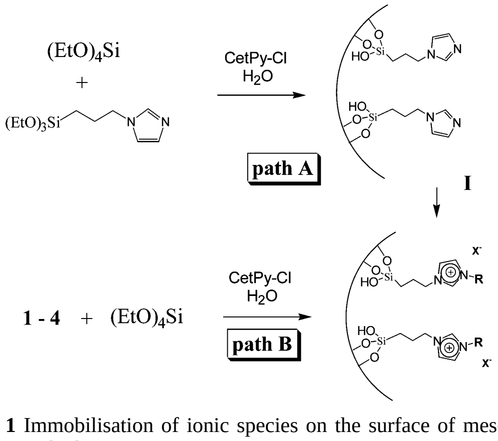
RTILs have been shown to be suitable reaction media for numerous catalytic reactions. However, the heterogenisation of ionic liquids on solid support is highly desirable because of the ease of separation. The immobilisation on a silica surface is of particular interest and gave rise to the concept of supported ionic liquid catalysis (*silc*).[2] RTILs, adsorbed or grafted on silica support, were used in hydrogenations,[2a] hydroformylations[2b] and Friedel–Crafts acylations.[2c]

Our current interest in the elaboration of self assembled silica hybrid gels[3] led us to explore the synthesis of nanostructured silica hybrids containing ionic species. Nanostructured mesoporous materials attracted considerable interest during the last decade.[4] The immobilisation of functional organic fragments within an ordered mesoporous silica framework can be achieved *via* a template directed hydrolysis–polycondensation procedure.[5] In this paper, we report new nanostructured silica supported imidazolium species by two approaches:

- the post alkylation of ordered silica functionalized by imidazole units (Scheme 1, path A).
- the cocondensation of trialkoxysilylated alkylimidazolium halides with tetraethoxysilane (Scheme 1, path B).

These materials are of particular interest because of their regular, ordered architecture allowing high accessibility of the immobilized imidazolium units.

We first studied path A to reach imidazole containing nanostructured silica. A related material containing dihydroimidazole units has been described by Mann *et al.*[5c] 1-[3-(triethoxysilyl)propyl]imidazole was prepared by coupling imidazole and 3-chloropropyl-triethoxysilane.[6] An imidazole containing ordered silica hybrid material **I** was then prepared from TEOS and 1-[3-(triethoxysilyl)propyl]imidazole using cetylpyridinium chloride as a template. The XRD pattern of the resulting material **I** showed a set of peaks characteristic of a hexagonal silica mesophase (XRD: *d*-spacings: (100) 3.70 nm; (110) 2.12 nm; (200) 1.86 nm).



Scheme 1 Immobilisation of ionic species on the surface of mesoporous nanostructured silicas.

Alkylation of the pendant imidazole entities in **I** with various alkyl halides led to the formation of the materials **II**–**V** incorporating alkylimidazolium species (Scheme 1, path A).

Elemental analysis of the materials **II**–**V** showed that the alkylation of the imidazole rings occured quantitatively, indicating high accessibility of the supported imidazole groups. The created ionic species also showed good accessibility and reactivity. Bromination of the allyl groups in material **III** was successfully achieved leading to material **VI**. Nitrogen sorption experiments of materials **I**–**VI** revealed type IV isotherms and indicate that the hexagonal symmetry of the original imidazole functionalized silica was retained in the alkylated materials. Additionally, grafting of alkyl groups led to a decreasing pore diameter and, consequently, to a reduced specific surface of the materials **II**–**VI** (Table 1).

Transmission electron microscopy confirms the results of N_2 sorption experiments and XRD. TEM images show a regular hexagonal array of 2-D aligned channels. TEM image of material **II** is given as an example in Fig. 1.

In a second route, we studied the direct incorporation of ionic species in organized silica hybrid mesophases by a template directed hydrolysis–polycondensation of TEOS with triethoxysilylated ionic precursors (Scheme 1, path B). The imidazolium precursors **1–4** (Table 2) were prepared either by coupling 1-methylimidazole/1-allylimidazole with 3-chloropropyltriethoxysilane (precursors **1** and **2**) or by reacting 1-[3-(triethoxysilyl)propyl]imidazole with 1-bromohexane/1-bromododecane

Table 1 Results of nitrogen sorption experiments of the imidazole functionalized silica **I** and the post alkylated materials **II**–**VI**

Material	Grafted halide	BET surface area/m² g⁻¹	Pore volume/ mL g⁻¹	Pore diameter/nm
I	—	1088	0.79	2.9
II	CH_3I	984	0.70	2.8
III	CH_2=CH–CH_2Br	830	0.56	2.7
IV	$C_6H_{13}Br$	814	0.53	2.6
V	$C_{12}H_{25}Br$	765	0.51	2.6
VI	**III** after addition of Br_2	709	0.44	2.5

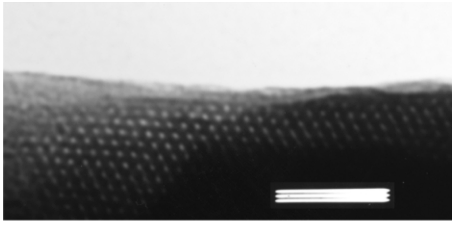


Fig. 1 TEM micrograph of material **II** (space bar: 25 nm).

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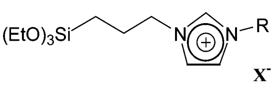
Table 2 Trialkoxysilylated ionic precursors used in this study

	Precursor	R	X
	**1**	CH_3	Cl
	2	$CH_2–CH=CH_2$	Cl
	3	C_6H_{13}	Br
	4	$C_{12}H_{25}$	Br

(precursors **3** and **4**).† Contrarily to the non-silylated imidazolium halides which are crystalline solids at room temperature, the precursors **1–4** are viscous oils.

The materials **VII–X** were prepared from alkaline mixtures containing TEOS, an ionic organotriethoxysilane **1–4**, water, ammonia and the surfactant hexadecyl pyridinium chloride in the molar composition 0.9 : 0.1 : 114 : 8 : 0.12. The resulting mixtures were heated to 80 °C for 48 h. The surfactant was removed by repeated washing with acidic ethanol and the materials were finally dried at 110 °C for 24 h.

The incorporation of the organic entities within the silica network was monitored FT-IR and ^{13}C-CP-MAS spectroscopy and quantified by elemental analysis.

Nitrogen sorption experiments of **VII–X** reflect the formation of mesoporous silica hybrids. However, the sorption isotherms of **VII–X** indicated different types of mesostructured materials. Slight hysteresis loops in the sorption curves and decreased BET surface area values (Table 3) point to lamellar architectures of materials **VII** and **VIII**. In contrast, the sorption curves of the material **X** show typical type IV isotherms suggesting ordered silica mesophases with pore diameters of 2.3 nm. The sorption isotherms of the materials **VII** and **X** are represented in Fig. 2.

The characterisation of the solids by XRD confirms the different morphologies in the series of the materials **VII–X**. The X-ray diffractograms of the materials **VII–IX** showed only the (100) and (200) reflections, characteristic for materials with lamellar structures. However, these materials appear less ordered than those obtained by the grafting route (path A) (Fig. 3a). In contrast, the (100), (110) and (200) reflections in the pattern of the material **X** indicate a material with a well-defined hexagonal architecture (Fig. 3b). The *d*-spacings from the diffractograms of the materials **VII–X** are represented in Table 3.

The materials prepared by this cocondensation approach showed different morphological structures depending on the silylated imidazolium salt used. Whereas materials incorporating imidazolium salts with rather short alkyl substituents (methyl, allyl) showed lamellar structures, longer alkyl groups grafted on the imidazolium ring led to nanostructured silica hybrid materials with hexagonal symmetry. A modification of the micellar arrangement of the surfactant molecules in the hydrolysis condensation mixture may account for the observed changes in the material structure. Whereas the hydrophilic methyl- and allylimidazolium cations interact only with the polar head of the surfactant molecules, the dodecylimidazolium cation containing a hydrophobic hydrocarbon chain can behave as an amphiphilic molecule and may be incorporated in the micellar arrangement.

Table 3 Trialkoxysilylated ionic precursors used for the synthesis of the materials **VII–X**

			XRD *d*-spacings/nm		
Material	Used precursor	BET surface area/m^2g^{-1}	100	110	200
VII	**1**	415	5.55	—	2.74
VIII	**2**	502	6.41	—	3.24
IX	**3**	734	4.78	—	2.83
X	**4**	853	4.62	2.68	2.32

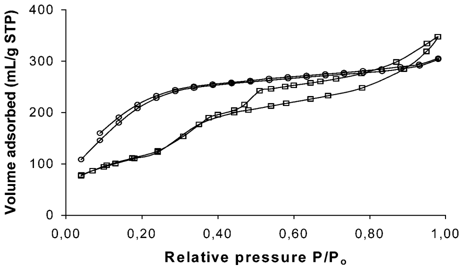


Fig. 2 N_2 sorption curves of the materials **VII** (□) and **X** (○).

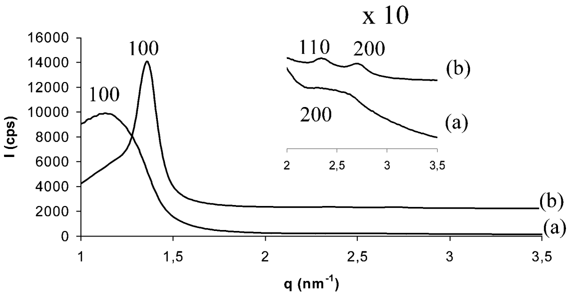


Fig. 3 XRD patterns of the materials **VII** (a) and **X** (b).

In conclusion, the incorporation of various ionic species in nanostructured mesoporous silica was achieved either (i) by grafting alkyl groups on ordered silica-immobilized imidazole units or (ii) by a direct hydrolysis–polycondensation of tetraethoxysilane (TEOS) with various triethoxysilylated alkylimidazolium halides in the presence of a structure directing agent. These ordered materials containing ionic species within the pore structures are of interest as support for the immobilisation of metallic species for the elaboration of supported ionic liquid catalysts (*silc*).

Notes and references

† All new compounds gave sufficient analytical and spectroscopic data, *e.g.* 1-allyl-3-[3-(triethoxysilyl)propyl] imidazolium chloride **2**: ^1H NMR (DMSO-d_6): δ 0.51 (m, 2H), 1.13 (t, 9H, J = 7.2 Hz), 1.83 (m, 2H), 3.74 (q, 6H, J = 7.2 Hz), 4.17 ('t', 2H), 4.85 (m, 2H), 5.38 (m, 2H), 6.01 (m, 1H), 7.75 (s, 1H), 7.85 (s, 1H), 9.21 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 6.6, 18.1, 23.5, 50.8, 51.1, 57.8, 120.0, 122.5 (2C), 131.7, 136.0; ^{29}Si NMR (DMSO-d_6) −46.4; *m/z* [FAB+] (%) 313 (100) (1-allyl-3-[3-(triethoxysilyl)propyl] imidazolium cation).

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