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SiO_2 units networking through ionic liquid-like bridges

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Abstract Hybrid organic-inorganic silica-based materials containing bridging ionic liquid-like entities were prepared, from 1,3-di(3-trimethoxysilylpropyl)-imidazolium iodide and tetraethoxysilane. The final material is characterized by a high thermal stability. TEM micrographs of the obtained hybrid material allow its comparison with silica nanoparticles bridged through ionic liquid-like links.

Keywords Sol–gel; Hybrid material; Modified ionic liquid.

Introduction

Since ionic liquids present extremely interesting and uncommon properties [1–5] they are more and more investigated in association with metal oxides to yield new hybrid organic-inorganic materials. In the first approaches ionic liquids were used for the design of inorganic silica matrix. *Dai et al.* first reported the use of 1-methyl-3-butylimidazolium bis((trifluoromethyl)sulfonyl)amide as effective solvent to synthesize aerogels [6]. In this case the imidazolium ionic liquid plays the role of a template around which the silica matrix is built. Other studies investigated the possibilities of structuring the silica matrix morphology through ionic liquids [7], as reported by *Antonietti et al.* [8, 9].

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Going a step further led to use the silica based material entrapping the ionic liquid. Thanks to this approach ionic liquid templated periodic mesoporous organosilica materials [10] were further used for designing anion exchange resins [11], being solid thanks to the silica matrix and additionally possessing the properties of the genuine ionic liquid. The targeted applications were catalysis [12] or conductivity [13, 14] for example.

Developing new catalysts based on silica and ionic liquids drove to the design of ionic liquid functionalized silica gels [15, 16]. Those new materials proved to be effective and recyclable catalysts, in some cases not even requiring an additional organic solvent [17]. High performance liquid chromatography systems were also developed by functionalizing silica with 1-alkyl-3-(propyl-3-sulfonate)imidazolium [18] or 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium tetrafluoroborate [19] to obtain a zwitterionic stationary phase.

Imidazolium species are versatile precursors for the generation of N-heterocyclic carbene complexes [20]. Thus, a bis-silylated imidazolium compound, namely 1,3-di(3-triethoxysilylpropyl)imidazolium iodide, was used as silica precursor for designing heterogeneous catalysts for *Mizoroki-Heck* reactions [21]. Silica modified through a bis-silylated imidazolium species was used to capture palladium nanoparticles onto spherical silica nanoparticles [22].

For the design of such new organic-inorganic hybrid materials including ionic liquid-like molecules, we recently published an approach to the linking of

silica nanoparticles through an ionic liquid-like network [23]. The synthesis was based on the use of preformed silica nanoparticles. In this paper we compare these materials with hybrid materials prepared by sol-gel processing from a $Si(OR)_3$-modified ionic liquid with $Si(OR)_4$.

Results and discussion

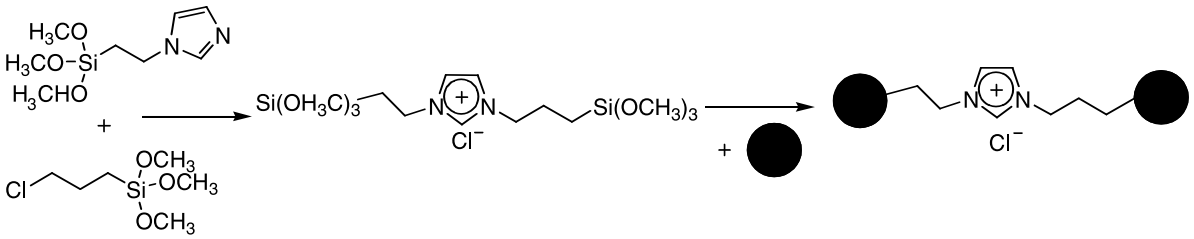
Linking silica nanoparticles through ionic liquid-like network

The method used previously to obtain a silica nanoparticle network was the modification of preformed SiO_2 nanoparticles [24] by alkoxysilane ligands with ionic liquid-like groups [25]. For this purpose *Stöber*-like silica nanoparticles [24] were first synthesized, with a diameter of 20 nm [23]. The first possibility to connect the SiO_2 nanoparticles, Method A, deals with the use of an ionic liquid-like trimethoxysilyl-modified ligand (Scheme 1; black circles denote nanoparticles).

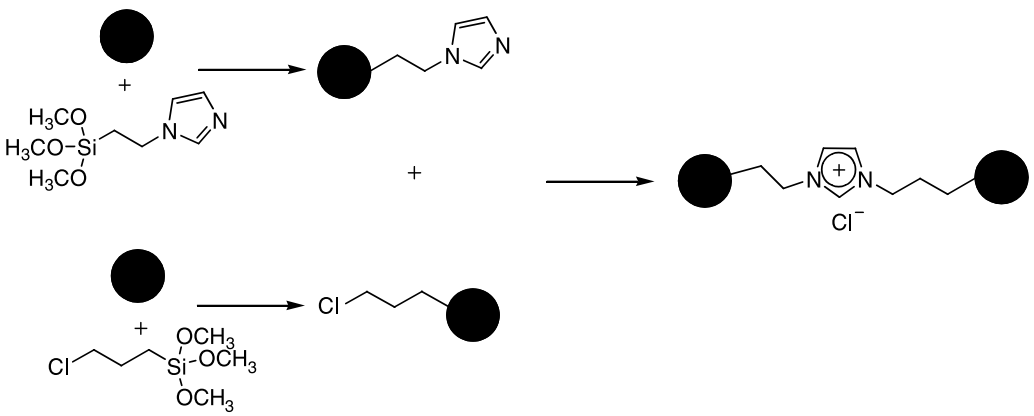
In Method B, the pre-formed silica nanoparticles were modified with either 3-chloropropyltrimethoxysilane or with *N*-(3-trimethoxysilylpropyl)imidazole [26] resulting in two different nanoparticles dispersions. The two dispersions were then mixed with each other, in a one to one ratio, allowing a nucleophilic substitution to occur between the ligands (Scheme 2).

The silica nanoparticles modified with chloropropyl ligands start to decompose around 120°C by degradation of the organic ligand (thin line in Fig. 1A). The silica nanoparticles modified by propylimidazol ligands are more stable, and start to degrade around 250°C (thick line in Fig. 1A). The thermal stability profile of the compound, obtained either by Method A or by Method B, shows a mass change occurring around 300°C (indicated by the vertical line in Fig. 1B). The thermal stability of the resulting compound is much higher than the one of the starting modified silica nanoparticles. This is a clear proof that the dialkylimidazolium halide link is formed, the ionic liquid-like molecules having a higher thermal stability than the corresponding organic groups used for their formation.

Thermal degradation of the organic part of the resulting linked nanoparticles takes place from 300 to 500°C. Above 500°C, only silica is remaining, corresponding to around 58 wt% of the material.



Scheme 1



Scheme 2

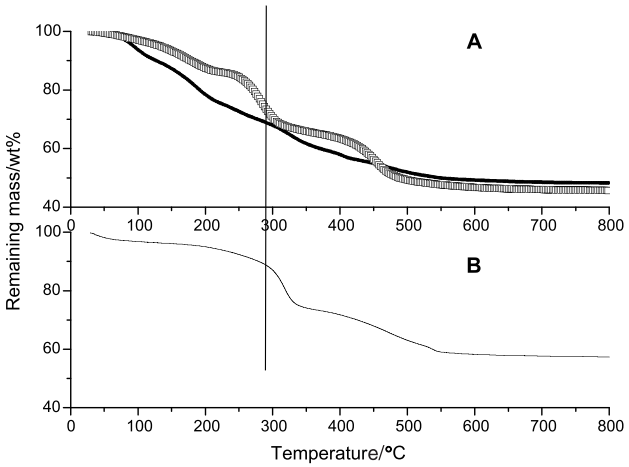


Fig. 1 TGA analysis; A: (thin line) silica nanoparticles modified with chloropropyl ligands; (thick line): silica nanoparticles modified with propylimidazol ligands; B: linked nanoparticles (Method B)

The materials appear as made of linked nanoparticles (Fig. 2). With Method A it seems that only few nanoparticles are linked with one another, as the diameters of the network structures are around 100 nm (circle in Fig. 2, left). With Method B, when nanoparticles are first modified, the nanoparticles networks are much bigger (Fig. 2, right).

The TGA proved that the imidazolium link is intact, and ^{29}Si and ^{13}C NMR spectra provided evidence that the silica particles were linked by the imidazolium groups. Thus, it is possible to affirm that the TEM presented above corresponds to connected nanoparticles and not to nanoparticle agglomeration.

In situ formation of SiO_2 structures

In Methods A and B, pre-formed silica particles, prepared by the *Stöber* process, were used. In the approach reported in this article, the silica structures were prepared *in situ*, in the presence of the linking ionic liquid 1,3-di(3-trimethoxysilylpropyl)-imidazolium iodide, under similar reaction conditions (Scheme 3).

Characterization of the obtained material by means of TGA (Fig. 3) shows a thermal degradation beginning around 300°C, what is only possible with an intact imidazolium link in the final material. The thermal degradation profile of the material is similar to the one obtained by the other methods (Fig. 1).

This is confirmed by a ^{13}C CP MAS NMR spectrum (Fig. 4) where the characteristic peaks of the link are still observable: at 126 and 116 ppm are the signals from the three imidazolium ring carbon atoms. The broad signal at 45 ppm corresponds to the very few methyl groups that remain in the product but mainly to residual methanol used as solvent. The peak area of those O–CH_3 groups, as evaluated

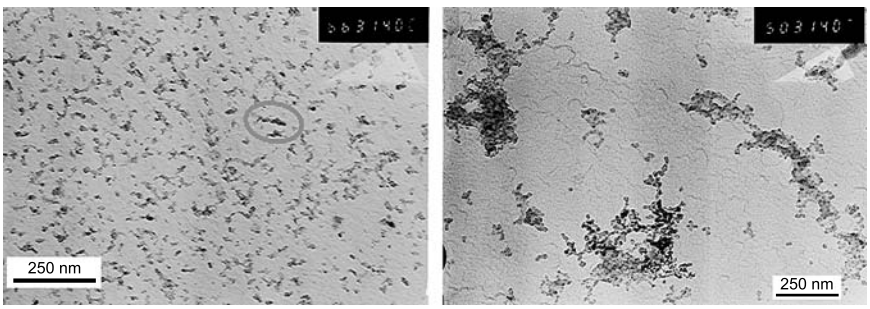
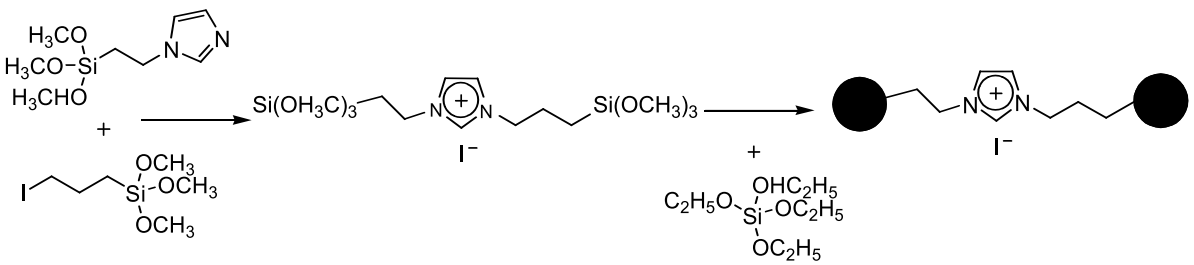


Fig. 2 TEM of the linked nanoparticles obtained by: (left) Method A; (right) Method B



Scheme 3

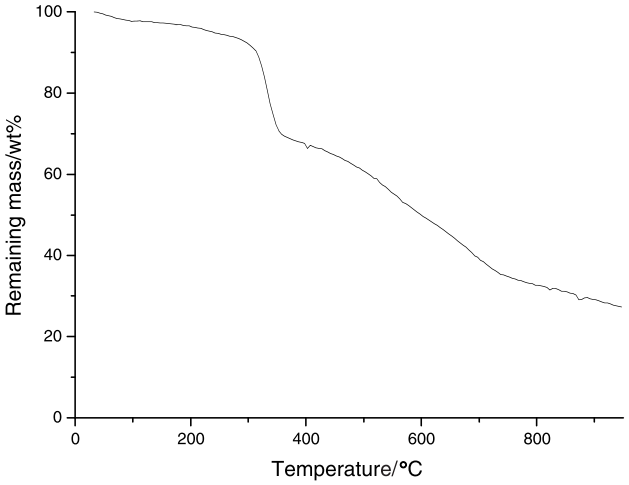


Fig. 3 TGA of the material obtained after *in situ* hydrolysis-condensation of *TEOS* in the presence of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (Method C)

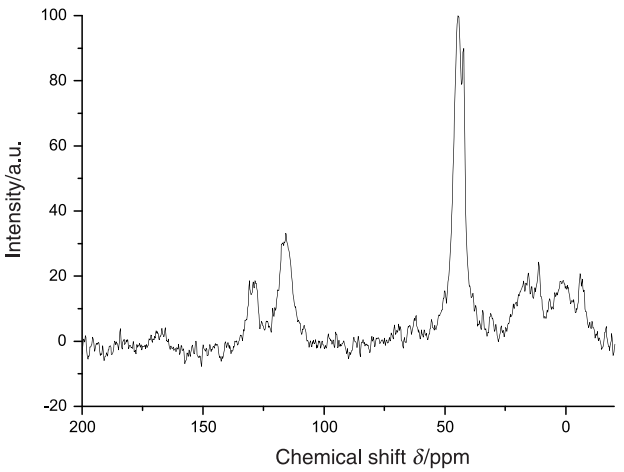


Fig. 4 CP MAS ^{13}C NMR spectrum of the material obtained after *in situ* hydrolysis-condensation of *TEOS* in presence of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (Method C)

through cross-polarisation method, is largely overestimated as the concerned carbon atoms are surrounded by much more hydrogen atoms than the other carbon atoms of the molecule. The three remaining signals between 5 and 18 ppm correspond to the carbon atoms of the alkyl chain between the nitrogen and the silicon atoms.

To investigate the efficiency of the sol–gel reaction a CP MAS ^{29}Si NMR experiment was carried out on the final powder (Fig. 5). The region around −70 ppm refers to the condensed trimethoxysilane groups, and the region around −120 ppm corresponds to the Q units from *TEOS*.

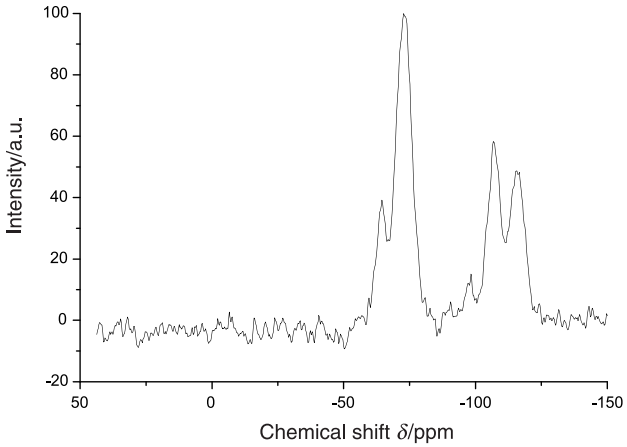


Fig. 5 CP MAS ^{29}Si NMR spectrum of the material obtained after *in situ* hydrolysis-condensation of *TEOS* in presence of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (Method C)

For Methods A and B as well as for Method C (Fig. 5) the MAS ^{29}Si NMR spectra were recorded using cross-polarization. As indicated for the precedent CP MAS ^{13}C NMR spectrum, cross-polarization has the consequence that, in every case, the Q_4 resonances (at −116 ppm, Si with no CH on the β position) are underestimated. Nevertheless the integrations are comparable from one spectrum to another one, even if a quantitative evaluation is not possible. From this comparison it appears that the Q_2 units (−97 ppm) are present in an equivalent proportion for every method. But the Q_3 peak (at −106 ppm) is higher for Method C than for the Methods A and B, while the Q_4 signal (at −116 ppm) is smaller for Method C. This is the clear proof that

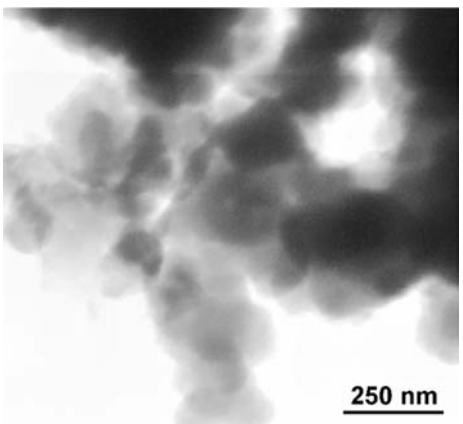


Fig. 6 TEM of the material obtained after *in situ* hydrolysis-condensation of *TEOS* in presence of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (Method C)

the *TEOS* precursor, used in Method C, is not condensed as well as with the precedent methods (A and B), where the *TEOS* condensation took place during the preparation of the particles.

In the TEM micrograph of the product obtained by Method C (Fig. 6), it is no longer possible to clearly distinguish silica nanoparticles. The material consists in domains around 100–150 nm.

Comparison of the three methods

With the Methods A and B previously reported, we can affirm the presence of ionic liquid-like links between the silica nanoparticles. The extension of the network made of connected nanoparticles is bigger with Method B, where nanoparticles were first modified. The limitation of the network dimensions for Method A comes from the various possibilities for the bis-silylated imidazolium to "back-bite".

In the case of Method C, where the bis-silylated imidazolium species were reacted with *TEOS*, the observed structures are quite big, having an average size of around 100–150 nm and a different morphology. Indeed, for Method C a silica network is formed instead of nanoparticles, as for Methods A and B, even if the *pH* conditions used were the same. By *in situ* reaction of *TEOS* and the bis-silylated imidazolium species, the morphology of the material is comparable to the one reported for materials deriving from the reaction of pure non-rigid bis-silylated species [27–29].

In, conclusion, the three methods we developed proved to be efficient to introduce ionic liquid-like connections between silica units. All the obtained materials are hybrid organic-inorganic possessing a high thermal stability, around 300°C.

Experimental

Chemicals

All the starting materials were reagent grade and used as purchased. Tertraethoxysilane (*TEOS*) was purchased from Fluka, chloropropyltrimethoxysilane from ABCR, and sodium iodide, imidazol, and methanol were obtained from Aldrich.

Measurements

Nuclear magnetic resonance (NMR)

Solution NMR spectra were recorded on a *Bruker* Avance 300 (1H at 300.13 MHz) equipped with a 5 mm inverse-broadband probe head with a z-gradient unit. Solid state NMR spectra were recorded on a *Bruker* DPX 300 (^{13}C at 75.40 MHz, ^{29}Si at 59.65 MHz) equipped with a 4 mm broadband MAS probe head. 13C and 29Si spectra were recorded with ramped CP MAS technique (Cross Polarization and Magic angle spinning).

Transmission electron microscopy (TEM) measurements

Samples for transmission electron microscopy measurements were prepared by dispersing the particles in ethanol prior to deposition on a carbon coated TEM Cu grid. TEM measurements were performed on a JEOL JEM-200CX or a JEOL JEM-100CX (USTEM, Vienna University of Technology).

Thermogravimetric analysis (TGA)

The analyses were carried out with a Shimadzu TGA-50 at heating rates of 5°C min^{-1} under air.

Synthesis

The syntheses of 3-iodopropyltrimethoxysilane, silica nanoparticles modified with either chloropropyltrimethoxysilane, *N*-propylimidazol, or 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide as well as the protocol for the nucleophilic substitution between chloropropyl modified silica nanoparticles and *N*-propylimidazol modified nanoparticles were reported previously [23].

In situ formation of SiO_2 nanoparticles (Method C)

This synthesis is carried out under argon. Under stirring, 60 mm^3 (10 mmol) of ammonia solution (32%), 90 mg (5 mmol) of water, and 0.418 g (2 mmol) of tetraethoxysilane (*TEOS*) are added to 0.526 g (1.011 mmol) of 1,3-di(3-propyltrimethoxysilane)imidazolium iodide dissolved in 15 cm^3 absolute methanol. The final solution is stirred for three days at ambient temperature. The suspension is then centrifuged, and the white solid is washed several times with methanol before drying under vacuum (3 mbar).

Acknowledgement

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