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Functionalisation of mesoporous silica nanoparticles with 3-isocynatopropyltrichlorosilane

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ABSTRACT

The functionalisation of Mesoporous Silica Nanoparticles (MSN) with the isocyanate group was carried out. The excellent reactivity of 3-isocynanatopropyltrichlorosilane allowed its grafting on the surface of MSN in mild conditions. Further reaction with different nucleophiles bearing primary amino groups led to the formation of a urea linkage and thus the covalent grafting of the nucleophiles to the MSN surface.

RÉSUMÉ

La fonctionalisation de nanoparticules de silice mésoporeuses (MSN) avec un groupement isocyanate a été entreprise. La réactivité excellente du 3-isocyanatopropyltrichlorosilane a permis son greffage à la surface des MSN dans des conditions douces. La réaction de l'isocyanate avec des nucléophiles possédant un groupement amine primaire a conduit à un lien urée et ainsi à l'ancrage covalent du nucléophile à la surface des MSN.

1. Introduction

Mesoporous Silica Nanoparticles (MSN) have attracted considerable interest in life and materials science [1–6]. Their unique properties such as high specific surface area (800–1000 m^2g^{-1}), monodisperse diameters (50–200 nm) and tunable pore size (2 to 4 nm) offer a large scope of applications such as drug delivery [7–11], photodynamic therapy [12–14], MRI [15–18], cancer cells targeting [19–21], catalysis [22,23], antireflective coatings [24]... The functionalization of MSN is the subject of tremendous efforts and many different functions such as amine [12], epoxide [25] or thiol [26] are routinely used with MSN to construct more complex structures. In this field, the isocyanate function has also been used with the condensation of isocyanatopropyltriethoxysilane to the mesoporous silica framework. However, as shown by Radu et al. [27], the conditions of the condensation of the triethoxysilane moiety (toluene at high temperature) affects the isocyanate group with the partial hydrolysis of this later. To avoid this drawback, we turned to 3-isocyanatopropyltrichlorosilane as the reagent of choice. Indeed we have previously shown that 10-isocyanatodecyltrichlorosilane was suitable for the preparation of isocyanato-functionalized self-assembled monolayers on silicon wafers without alteration of the isocyanate function [28–31]. We now present our work on the functionalization of MSN using isocyanatopropyltrichlorosilane and the subsequent reactivity of the isocyanate function with different nucleophiles.

2. Results and discussion

Isocyanatopropyltrichlorosilane was synthesized by hydrosilylation of allylisocyanate with $HSiCl_3$ using

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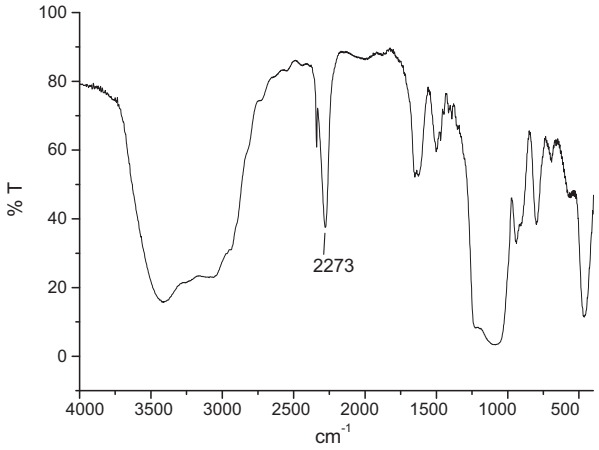


Fig. 1. IR spectrum of isocyanate group grafted on Mesoporous Silica Nanoparticles (MSN) (KBr pellet).

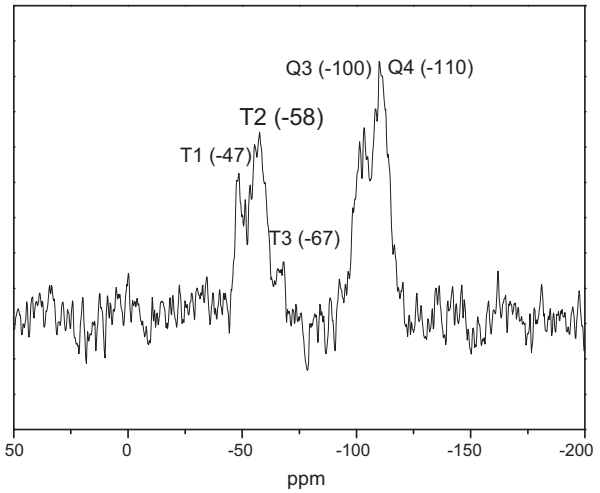


Fig. 2. Solid-State ^{29}Si DP MAS NMR of Mesoporous Silica Nanoparticles (MSN) functionalized with isocyanatopropyltrichlorosilane and dodecylamine.

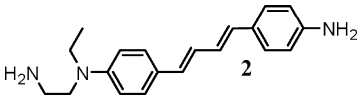
Karstedt's catalyst [28]. Isocyanatopropyltrichlorosilane was then grafted on the surface of MSN at RT in toluene or trichloroethylene in the presence of an excess of diisopropylethylamine, to lead to isocyanate-functionalized MSN. Diisopropylethylamine is necessary to trap HCl in order to avoid its subsequent addition to the isocyanate group. After 1 h, an aliquot was centrifuged in order to analyze the reaction. The isocyanate function was detected at 2273 cm^{-1} on the IR spectrum (KBr pellet, Fig. 1).

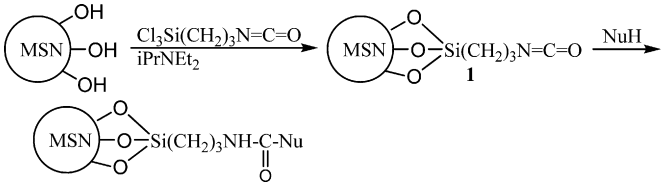
Thus, the reaction was much faster than with isocyanatopropyltriethoxysilane which required 12 h at the reflux of toluene for its grafting at the surface of MSN [27]. This isocyanate function of precursor **1** (Scheme 1) was particularly prompt to hydrolysis, thus the subsequent reactions were carried out without isolation of the nanoparticles. To assess the accessibility of the isocyanate on the surface and its reactivity, nucleophiles bearing primary amino groups were used. (Scheme 1).

Aliphatic or aromatic nucleophiles reacted with isocyanate-functionalized MSN overnight. Nanoparticles were isolated by centrifugation, washed with EtOH. IR spectra (KBr pellets) showed a total disappearance of the isocyanate function and the formation of a urea bond as attested by amide I and amide II bands (Table 1).

Solid-state ^{29}Si direct polarization (DP) MAS NMR showed that the condensation method led to T3 (minor), T2 and T1 (major) species, in agreement with a covalent anchoring of the trichlorosilane group on the MSN surface. A representative spectrum is presented in Fig. 2.

Table 1
Data of the Mesoporous Silica Nanoparticles (MSN) after reaction with isocyanatopropyltrichlorosilane and subsequent addition of NuH to the isocyanate function.

NuH	Amide I (cm^{-1})	Amide II (cm^{-1})	Specific Surface Area (m^2g^{-1})	Loading (mmol/g)	DLS before grafting (nm)	DLS after grafting (nm)
p-Toluidine	1646	1556	294	1.80	168	225
p-Anisidine	1650	1556	204	1.75	162	219
Dodecylamine	1695	1540	464	1.10	168	244
Butylamine	1691	1540	208	1.30	159	205
BOC-hydrazine	1687	1540	295	1.40	168	221
	1650	1556	434	0.86	162	351



Scheme 1. Reaction of Mesoporous Silica Nanoparticles (MSN) with isocyanatopropyltrichlorosilane to form precursor **1** and subsequent addition of nucleophiles.