

Grafting [60]fullerene on high surface area silica

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[60]Fullerene is grafted on high surface area silica using a hydrosilylation strategy based on prefunctionalization of the silica by (EtO)₂SiHMe, followed by reaction with [60]fullerene.

Catalysis has been envisaged as one of the various possible applications of [60]fullerene. Transition-metal complexes based on [60]fullerene have already been reported.¹ The use of such a complex in homogeneous catalysis for the hydroformylation of alkenes has also been described.² Organopalladium and -platinum polymers³ of [60]fullerene have been used as heterogeneous catalysts in the hydrogenation of alkenes and acetylenes. On the other hand, owing to strong metal-support interactions between Ni clusters and a multilayer film of [60]fullerene,⁴ as in the case of carbon nanotubes,⁵ [60]fullerene may be used as a new carbon support for metallic particles.

The rather low surface area [10–20 m² g⁻¹) and sublimation temperature of [60]fullerene limit its use as a support for heterogeneous catalysis. In order to avoid these problems, the covalent attachment of [60]fullerene to an inert support with a high surface area appears to be an interesting strategy. Based on the addition of an amino derivative as a connector, the grafting of [60]fullerene to silica has been reported.⁶ [60]Fullerene supported on metal oxides has also been achieved through osmium complexes.⁷

In order to anchor [60]fullerene on SiO₂, a stepwise strategy based on the prefunctionalization of SiO₂ by Si–H groups followed by a hydrosilylation reaction engaging [60]fullerene was employed.

Upon treatment of silica (Geduran SI 60, Merck, 506 m² g⁻¹, dried under vacuum at 150 °C for 24 h) with alkoxysilane, partially functionalized SiO₂ bearing Si–H groups on the surface was obtained. A suspension of silica in a mixture of diethoxymethylsilane–hexane (1 : 2) was heated to 60 °C under argon for 48 h. The resulting solid was washed with THF to remove unreacted alkoxysilane or its condensation product with moisture. The solid thus obtained was suspended in 1,2-dichlorobenzene containing both [60]fullerene and Pt⁰ as catalyst and heated to 125 °C under argon for 48 h. The brown solid isolated by filtration was washed with 1,2-dichlorobenzene until a clear supernatant was obtained. A mass increase was observed which appeared to be dependent upon the molar ratio of Pt⁰ to the generated Si–H groups.

The thermal behaviour was studied by thermal gravimetry under argon at 473–1123 K using a scan rate of 2 K min⁻¹. Under these conditions, a total mass loss of ca. 10% for the above-mentioned material was observed. Note that, under the same conditions, a mass loss of ca. 3.5% was obtained for the parent unfunctionalized silica. Furthermore, whereas in the case of the unmodified SiO₂, a smooth mass loss corresponding to the dehydroxylation of silanol groups leading to siloxane bridges was observed above 470 K, for the modified material a sharp mass loss, starting at 673 K and reaching a maximum at 930 K, was detected. Taking into account the mass loss due to physisorbed [60]fullerene below 673 K, the net mass loss

corresponding to grafted [60]fullerene was 5.5–6%. Based on the above-mentioned rather high transition temperature (930 K), it seems reasonable to assign the mass loss to an Si–C bond-breaking process corresponding to the release of the covalently linked [60]fullerene.⁸

In order to determine the surface area and pore size distribution using the BET and BJH methods respectively, adsorption–desorption experiments of N₂ at 77 K were carried out (Table 1). The pore diameter decreased from 4.6 nm for the unmodified SiO₂ to 4.0 nm for [60]fullerene-functionalized silica. This significant decrease of 0.6 nm appeared to parallel with the pore's volume and surface area. It seems likely that the decrease in porosity and in surface area results from the presence of [60]fullerene physisorbed and/or chemically bonded on the surface of silica.

The modification of silica was also investigated by FTIR spectroscopy. The IR spectra were recorded between 500 and 4000 cm⁻¹ after heating under vacuum at 673 K for 2 h. While for the unmodified SiO₂ the lattice and OH vibrations were observed at 2000 and 3745 cm⁻¹, respectively, for the [60]fullerene-modified material, in addition to the above-mentioned bands, other peaks corresponding to C–H (3000–2880 cm⁻¹), Si–H (ca. 2170 cm⁻¹), C–C and Si–C (1400–1200 cm⁻¹) vibrations were also detected. As expected, both characteristic bands⁹ of [60]fullerene at 526 and 1428 cm⁻¹ were observed. The IR study revealed the initial grafting of MeSiH(OEt)₂ (significant decrease in the OH bands intensity), and the presence of [60]fullerene on the surface. However, the presence of Si–H vibrations indicated that the reaction between [60]fullerene and the surface (SiO)₃Si–H groups was incomplete.

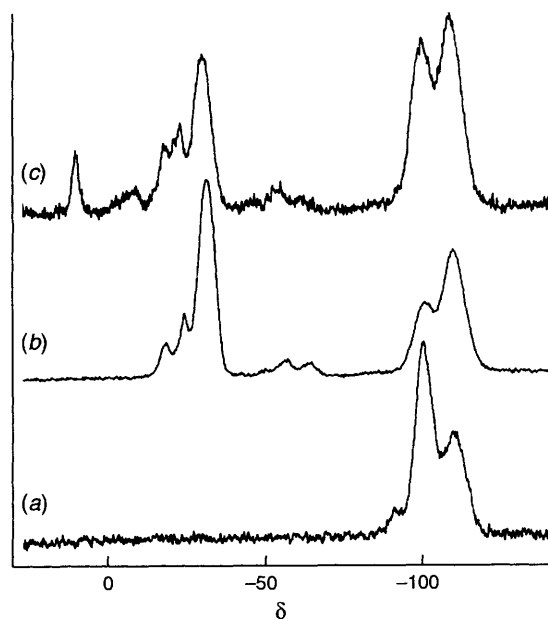
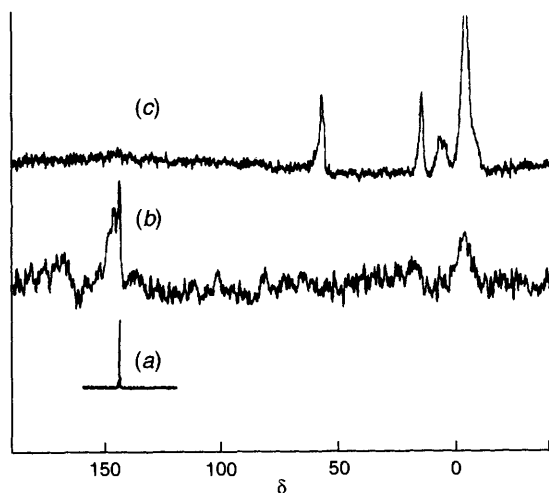
The ²⁹Si and ¹³C NMR spectra are given in Figs. 1 and 2, respectively, and the chemical shifts are collected in Table 2. For the parent SiO₂, three signals at δ –90.8, –101 and –109.7 corresponding to (SiO)₂Si*(OH)₂, (SiO)₃Si*(OH) and (SiO)₄Si*, respectively, were observed in the ²⁹Si spectra [Fig. 1(a)]. Upon condensation of MeSiH(OEt)₂ with SiO₂ [Fig. 1(b)], the intensity of the signals at δ –90 and –101 decreased significantly with respect to the signal at δ –109, indicating the conversion of Si–OH groups into Si–O–Si fragments. Furthermore, while for the parent SiO₂ no signal was detected between δ 0 and –70, for the functionalized material, six peaks between δ –15 and –70 were observed. These signals correspond to Si atoms of the types (SiO)Si*(H(Me))(OEt) and (SiO)Si*(H(Me))(OH) in different environments. With regard to the [60]fullerene-grafted material [Fig. 1(c)], in addition to the above-mentioned signals, a peak at δ 8.4 was observed. While the signals between δ –10 and –60 may be attributed to

Table 1 Textural characteristics of SiO₂ and SiO₂–C₆₀

Sample	Surface area/ m ² g ⁻¹	Pore diameter/ nm	Pore volume/ cm ³ g ⁻¹
SiO ₂	506	4.6	0.78
SiO ₂ –C ₆₀	393	4.0	0.52

Table 2 Chemical shifts for ^{29}Si and ^{13}C solid-state NMR spectroscopy

Sample	δ										
	^{29}Si NMR:										
SiO_2	-109.7	-101.0	-90.8								
$\text{SiO}_2\text{-SiH}$	-110.2	-101.0	-90.8	-63.7	-56.7	-50.4	-33.0	-25.4	-19.6		
$\text{SiO}_2\text{-C}_{60}$	-110.4	-101.7	-92.3	-63.7	-56.0	-47.7	-31.8	-25.0	-19.6	-10.7	8.5
	^{13}C NMR:										
$\text{SiO}_2\text{-C}_{60}$	2.3	6.2	8.1	16.1	58.4	143.5	146				

**Fig. 1** ^{29}Si MAS NMR spectra of SiO_2 (a), Si-H functionalized SiO_2 (b) and SiO_2 grafted with C_{60} (c)**Fig. 2** ^{13}C MAS NMR spectra of C_{60} (a) and $\text{SiO}_2\text{-C}_{60}$ (b): CP MAS NMR spectrum of $\text{SiO}_2\text{-C}_{60}$ (c)

unreacted Si-H groups, the presence of signals at higher field (δ -10.7 and 8.4), which may be assigned to conversion of MeSi-H into MeSi-C₆₀ sites, is a clear-cut argument in the favour of the addition of [60]fullerene to Si-H fragments.

In agreement with reported data,¹⁰ the ^{13}C MAS NMR study of [60]fullerene revealed a single sharp signal at δ 143.6 [Fig. 2(a)], implying the equivalence of all carbon atoms. In

marked contrast, for the immobilised [60]fullerene [Fig. 2(b)], in addition to a set of peaks between δ 2 and 8 corresponding to different types of Si-Me groups, a multicomponent broad signal between δ 140 and 150 was obtained. The disappearance of the latter signal in the ^{13}C CP MAS NMR [Fig. 2(c)] experiment indicated that it was due to quaternary carbons and therefore it was assigned to the [60]fullerene fragments. However, the ^{13}C CP MAS NMR experiment revealed two additional signals which may be assigned to unreacted SiOEt moieties and/or to addition products of alkoxy silane to the surface siloxane groups.¹¹ Moreover, it is worth noting that their intensity was substantially lower than the intensity of signals due to Si-Me groups, demonstrating the high degree of functionalization of silica.

In conclusion, using a variety of solid-state methods (TG, FTIR, NMR) we have demonstrated the covalent attachment of [60]fullerene to silica *via* a hydrosilylation reaction. The use of the above-mentioned material in heterogeneous catalysis is under current investigation and will be reported elsewhere.

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Footnotes

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