Mendeleev Commun., 1992, 2(2), 46–47

A Prospective Route for the Conversion of Si—O—C Bonds into Si—C in Chemisorbed Compounds

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The ≡Si—H groups in silica, prepared by thermolysis destruction of methylated silica, have been found to react with alk-1-enes to give Si—C bonds at the silica surface.

It has been shown previously that catalytic hydrosilylation may proceed not only in solution, but also by involving moieties attached to silica surfaces, *e.g.* ≡Si—H groups and alk-1-enes with various hydrocarbon chain lengths.[1] In this case ≡S—H groups were introduced into a surface silica layer using an appropriate chlorosilane (*e.g.* methyldichlorosilane). There is, however, another way to produce ≡Si—H groups on silica surfaces. It was first suggested in ref. 2 that such groups could be obtained by thermal decomposition of methylated silica. It is thought[3] that decomposition of the methoxy groups occurs predominantly as in eqn. (1). Subsequent hydrosilylation of the

$$\equiv\text{Si—OMe} \xrightarrow{\text{heat}} \equiv\text{Si—H} + \text{H}_2\text{C=O} \qquad (1)$$

grafted ≡Si—H groups with appropriate alkenes allows us to obtain a number of compounds silica-supported, containing Si—C bonds, without employing any organosilicon reagents. Direct experimental verification was also required for the transformation [eqn. (2)].

$$\equiv\text{Si—OMe} \longrightarrow \equiv\text{Si—H} \longrightarrow \equiv\text{Si—CH}_2\text{—CH}_2\text{—R} \qquad (2)$$

R = organic radical

Methylated silica were prepared by the same method as in refs. 4 and 5. The course of the chemical transformations in the surface silica layers was monitored with IR spectroscopy ('IKS-29' spectrophotometer, region: 4000–2000 cm^{-1}, Aerosil plates with $S_{spec} = 300\ m^2\ g^{-1}$, 20–30 mg, compacting pressure 1.72×10^8 Pa). The hydrosilylation reaction was carried out using a liquid-phase technique in oct-1-ene at its boiling temperature (121.6 °C) with 0.05 mol dm^{-3} H_2PtCl_6 in propan-2-ol as a catalyst. The alcohols and oct-1-ene were purified[6] and then dried using NaX molecular sieves.[7]

The silica, which was evacuated in advance at 400 °C [see Fig. 1(*a*)] was treated with methanol vapour at 380 °C until all the isolated silanol groups had reacted. Completion of the methanol chemisorption on the silica surface [Fig. 1(*b*)] was indicated by the occurrence of characteristic absorption bands corresponding to asymmetric and symmetric vibrations of the C—H bonds in the methoxy groups (ν_{max}/cm^{-1} 2955 and 2855, respectively) and by the absence of the absorption band corresponding to the isolated silanol groups (3750 cm^{-1}). On thermoevacuation of the methylated silica at 700 °C the absorption bands for the methoxy groups show a sharp decrease in their intensities in the IR spectrum. In addition, a strong absorption band at 2280 cm^{-1}, caused by valence vibrations of the Si—H bonds, together with a 3750 cm^{-1} band of moderate intensity now emerged [Fig. 1(*c*)]. In order to eliminate any side effects concerning the reappearance of the silanol groups, the surface was treated with hexamethyldisilazane vapours at 100 °C. This did not affect the intensity of the 2280 cm^{-1} absorption band, the IR spectrum being characterized by absorption bands due to valence asymmetric and symmetric vibrations of the C—H bonds in the grafted trimethylsilyl groups. The absorption band of isolated silanol groups was absent [Fig. 1(*d*)]. After completion of the hydrosilylation reaction [Fig. 1(*e*)] there is a considerable (90%) reduction in the intensity of the absorption band related to the Si—H groups. A characteristic weak absorption band at 2265 cm^{-1}, corresponding to the Si—H groups, still remained. Concurrently with elimination of the Si—H groups the intensities of absorption bands corresponding to valence vibrations of the C—H bonds in methylene (2930, 2855 cm^{-1}) and methyl (2980, 2900 cm^{-1}) groups increased.

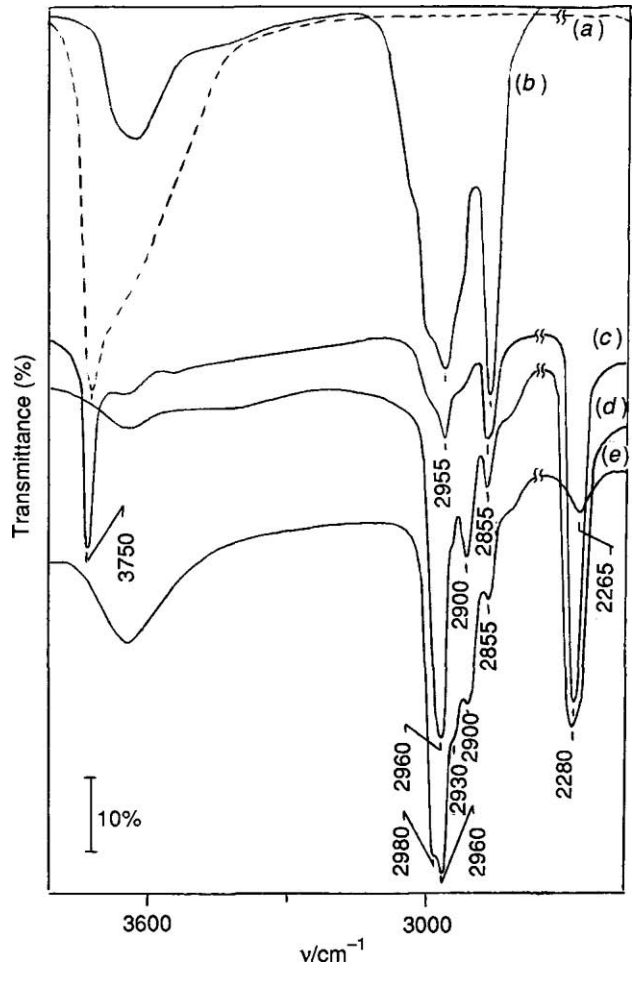

Fig. 1 IR absorption spectra for silica: evacuated at 400 °C over a period of 2 h (*a*); after treatment with methanol vapour at 380 °C for 3 h, and evacuation at 300 °C for 1 h (*b*); after thermal evacuation at 700 °C within 40 min (*c*); after treatment with hexamethyldisilazane vaours at 100 °C within 1 h and evacuation at 400 °C within 1 h (*d*); and after subsequent interaction with oct-1-ene and evacuation at 400 °C within 1 h (*e*).

The spectroscopic evidence suggests that the Si—H groups arising as a result of thermal decomposition of the methylated silica are transformed into chemically grafted hydrocarbon radicals. As a result, the proposed method may be used for the synthesis of organosilicas containing thermally and hydrolytically stable Si—C bonds between the silica surface and the organic functional groups, without using any organosilicon reagents.

Received: Moscow, 13th September 1991
Cambridge, 26th November 1991; Com. 1/05349C

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