# Siloxane Bridges as Reactive Sites on Silica Gel

Fourier Transform Infrared–Photoacoustic Spectroscopic Analysis of the Chemisorption of Diborane

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The reaction of diborane with the silica gel surface has been studied with Fourier transform infrared photo-acoustic spectroscopy (FTIR–PAS). After a dissociative adsorption of diborane on the siloxane bridges, borane reacts with the hydroxyl groups of the silica gel surface, evolving hydrogen gas. Besides this general reaction (a), a new reaction (b) is observed, which is competitive with the direct boranation of the hydroxyl groups. The siloxane bridges act as reactive chemisorption sites, resulting in the formation of silane groups.
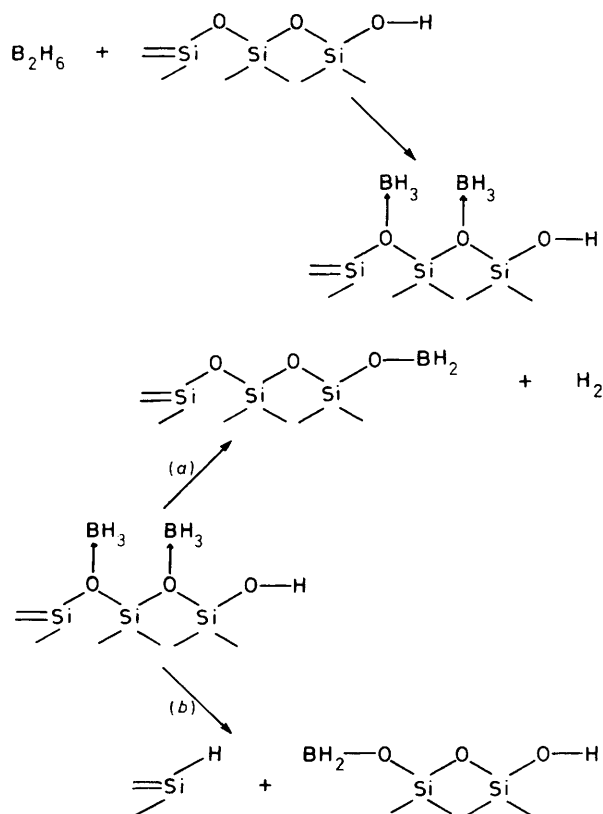
Silica gel is a porous, amorphous type of silica. The presence of hydroxyl groups and molecular adsorbed water dominates the surface chemistry of pure silica.[1] Hydration water and hydroxyl groups are present in different proportions, depending on the pretreatment temperature.[2–5] These compounds have been considered as the reactive sites on silica gel. Diborane, boron halides[6,7] and silanes[8–10] are frequently used as probes for the reactivity of the silica gel surface. Reactions of boron halides[6] and some silanes[9,11] seem to be hydroxyl specific and a distinction between the free hydroxyl groups and the bridged hydroxyl groups is achievable.

Diborane has often been used to determine the total hydroxyl content of the silica surface,[2,5,12] but diborane does not permit the distinction between hydration water and hydroxyl groups.[12] The following general reaction scheme can be proposed:[12–14] Prior to chemisorption a physical adsorption of diborane occurs on the siloxane bridges:[12,15]

(a) a physisorption of borane groups on the siloxane bridges after a symmetrical split of diborane molecule
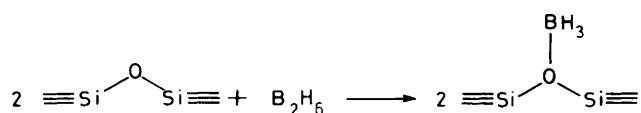

(b) a nucleophilic addition reaction of diborane, a direct physisorption of diborane on siloxane bridges, which can be accompanied by a cleavage of the physisorbed diborane
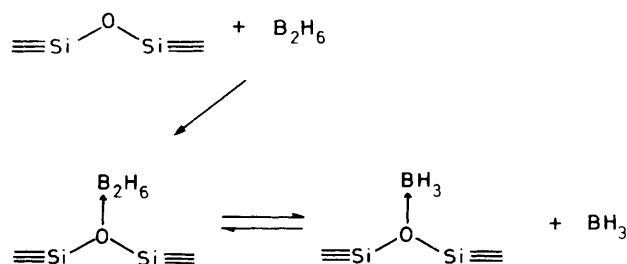
Hereafter two types of chemisorption reaction can occur: (a) a nucleophilic substitution reaction of hydroxyl groups with (physisorbed) borane, evolving hydrogen gas
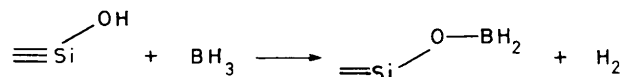
(b) furthermore a chemisorbed borane group can react with another hydroxyl group, evolving hydrogen gas
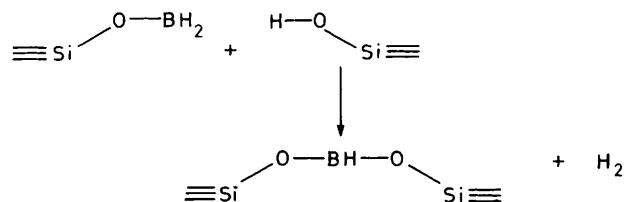
The reactivity of a hydroxylic surface, although not fully clarified, remains an important topic in catalysis and sorbent technology. The purpose of this investigation is to evaluate the current mechanism of the diborane chemisorption. FTIR–PAS, which is more appropriate for surface studies than common transmission FTIR, was used to achieve a clearer picture of the sorption of a reactive gas onto the hydroxylated silica gel surface.

Experimental

The silica gel sample was a Kieselgel 60 from Merck with a particle size between 0.040 and 0.063 mm. The specific area was 416 m^2 g^{-1} and the average pore size diameter is 6 nm (Kieselgel 60). Prior to the reaction with diborane, the silica gel was heated under vacuum conditions for 17 h at the desired temperature to remove water from the surface. Diborane, supplied as a 5% mixture in hydrogen gas (UCAR N.V.), was subjected to a cryogenic distillation before use. The boranation reaction occurred in a classic dynamic volumetric adsorption apparatus[16] to achieve quantitative results. Ca. 4 mmol of diborane was submitted to 1 g of degassed silica gel for 11.30 h at 65 °C. After reaction, a cryogenic separation removed the residual diborane. The amount of evolved hydrogen was measured with a mercury manometer and then evacuated. A prolonged cold-trap evacuation of the sample was executed, first to remove all physisorbed compounds off the surface and secondly to prevent damage to the PA cell. Thereafter, the degassed sample was transferred into a nitrogen-purged glove box. Under these dry conditions, the sample was loaded in the PA cell. The PA spectra were recorded at room temperature on a Nicolet 5DXB Fourier transform infrared spectrometer in the region 4000–400 cm^{-1} at a 4 wavenumber resolution. An average of 500 scans was used for the transformation and the mirror velocity was 0.08 cm s^{-1}. The PA detector is a prototype of the MTEC-100 cell, constructed by McClelland. The PA spectrum of carbon black was used as background.

Results and Discussion

The IR spectra obtained with PA detection, show more details compared to earlier published IR spectra of silica treated with diborane (Fig. 1 and 2). Fig. 1 displays the FTIR–PA spectra of silica gel degassed at 220 °C and treated with diborane. The amount of chemisorbed diborane was increased by enlarging the submitted amount of diborane. As the number of sorbed borane groups increases, the intensity of the free hydroxyl group vibration (3745 cm^{-1}) gradually diminishes and finally disappears at a chemisorption degree

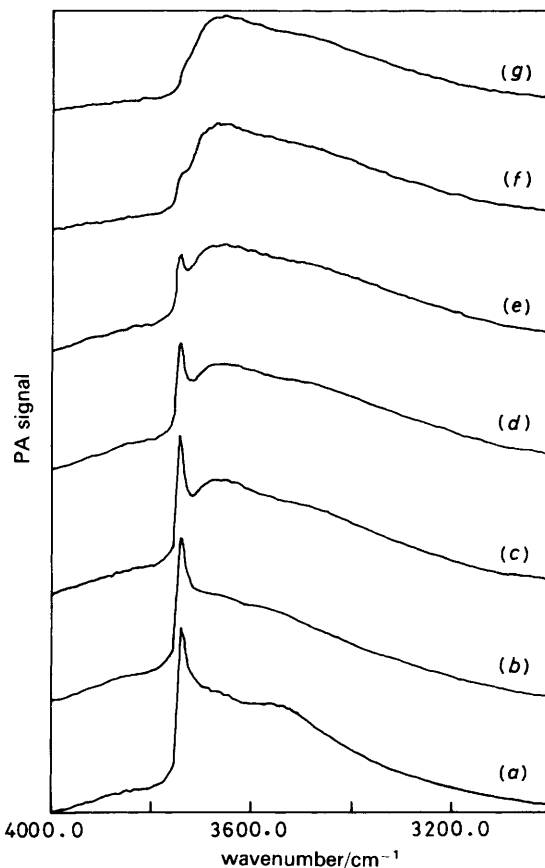Fig. 1 FTIR–PA spectra of silica gel, degassed at 220 °C for 17 h and treated with diborane at 65 °C. Amount of chemisorbed diborane (/mmol g^{-1} silica gel): (a) 0.00; (b) 0.25; (c) 0.64; (d) 0.75; (e) 0.97; (f) 1.00; (g) 1.21

greater than 1.00 mmol diborane per g silica gel. The residual absorption band (3600–3300 cm^{-1}) in the OH stretching region indicates that some unreactive hydroxylic species (bridged hydroxyl groups and eventually molecular adsorbed water) remain on the surface. Inner hydroxyl groups and molecular water, still present in the structure at this dehydration temperature[5,17] and inaccessible for diborane, are thought to cause this residual absorption band.

The amount of evolved hydrogen is a measure for the hydroxyl content of the surface, regardless of their surface mode. The experimentally obtained hydroxyl content of the silica gel surface, 5.2 OH nm^{-2}, is slightly higher than the generally accepted 5.0 OH nm^{-2}.[18] Although an IR absorption due to inner hydroxyl groups is observable, all the surface hydroxyl groups have reacted.

Owing to the PA detection, the spectral sensitivity is enhanced (Fig. 2). The absorption maxima in the boron–hydrogen stretching region are those cited in earlier papers.[12,14,15,19,20] Infrared bands of physisorbed (di)borane (e.g. 1665 cm^{-1}) were not observed and owing to the evacuation procedure, other gaseous or physisorbed boron–hydrogen compounds are unlikely. However, a vibration band, located at 2270 cm^{-1}, has never been observed or mentioned in the literature. Many references[21,22] cite boron–hydrogen IR bands of ionic and gaseous boron compounds, but a boron–hydrogen stretching vibration of a covalently bonded boron compound has never been observed at such a low wavenumber, not even in boron–nitrogen compounds.[23,24] Comparison of infrared library data,[20,21,25] and literature of similar work[26,27] with our own results,[11] suggests another surface compound (≡Si—H). So it must be
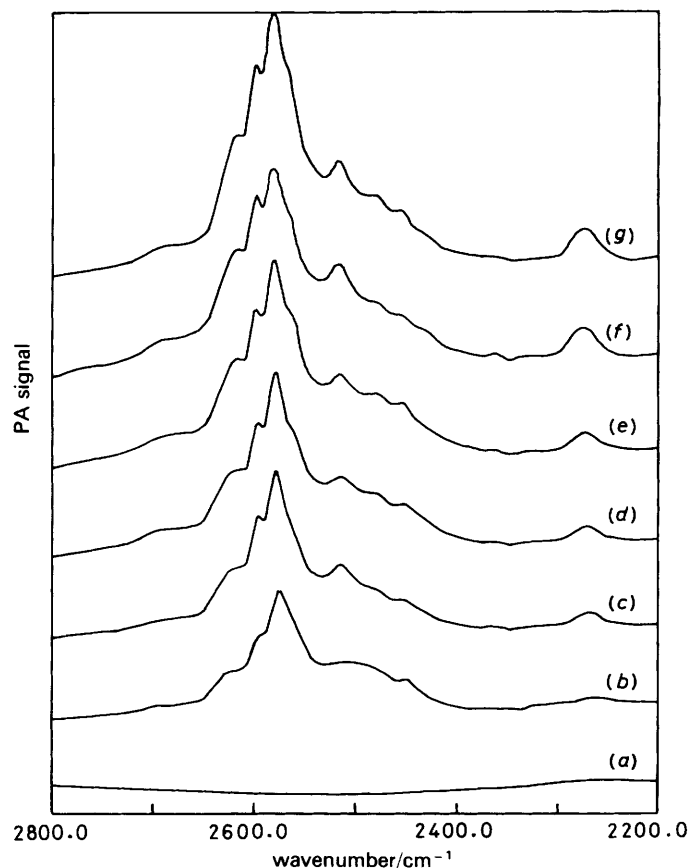
Fig. 2 FTIR–PA spectra of silica gel, degassed at 220 °C for 17 h and treated with diborane at 65 °C. Amount of chemisorbed diborane (/mmol g^{-1} silica gel): (a) 0.00; (b) 0.25; (c) 0.64; (d) 0.75; (e) 0.97; (f) 1.00; (g) 1.21

assumed that a side reaction occurs on the silica gel surface, resulting in the formation of a silane group. Because no reaction of (di)borane with hydroxylic species is known to result in a silane bond, a siloxane bridge should be the reactive site. Surface siloxane bridges were already proposed as physisorption sites,[12,15] but never reported as potentially reactive chemisorption sites.

Further evidence can be obtained by spectral band integration. An integration of a spectral region was carried out with an internal reference band.[28] Following the suggestions of Gardella et al.[29] and Gorski et al.,[8] a photo-acoustic unsaturated band was chosen as reference, more specifically a $\equiv$Si—O—Si$\equiv$ combination band (1860 cm^{-1}). The integration value of the boron–hydrogen vibration region as a function of the sorbed amount of diborane is not highly correlated with the integration value of the silane band. As a result, the reactive surface sites should be different from the hydroxyl groups. The following mechanism is proposed
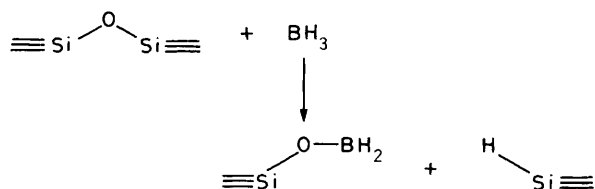
Kinetic experiments confirm this reaction mechanism. Evaluation of the results excludes a monomolecular and bimolecular reaction. The best fit is obtained for a bimolecular competitive reaction. The gaseous reaction species in the reaction scheme is borane. Two different reactive compounds are found on the surface, i.e. hydroxyl groups and siloxane bridges
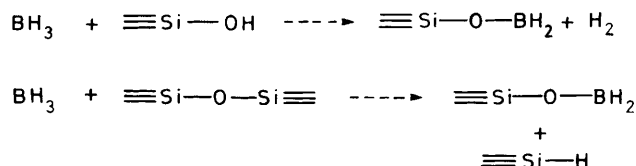
This reaction scheme explains the observed silane band. The proof for a bimolecular competitive reaction is a linear relationship of the ratio H_2/SiH as a function of reaction time. The number of silane species can be estimated by the integration of the silane band. The ratio H_2/SiH vs. time is linear ($r = 0.95$; Fig. 3). An estimation of the reaction rate of the proposed competitive reaction is only possible when the concentration of hydroxyl groups and (reactive) siloxane bridges is known.

Introducing a different number of surface siloxane bridges and hydroxyl groups should affect the ratio H_2/SiH. Progressive dehydration and/or dehydroxylation of a silica gel will enlarge the relative concentration of the surface siloxane bridges. Experiments with boranated silica gel, pretreated at different temperatures, confirm the proposed reaction mechanism. The ratio H_2/SiH decreases linearly (Fig. 4). Morrow and co-workers[27,30,31] stated that a site of unusual chemical activity can be generated by degassing silica at elevated temperatures. The new sites are strained siloxane bridges (infrared bands: 908 and 888 cm^{-1}) and react by means of the same mechanism as proposed in this paper. However the characteristic infrared bands of the new sites were not observed. Neither is the appearance of the sites evidenced by chemisorption data. A higher pretreatment temperature favours the boranation of siloxane bridges, instead of the direct boranation reaction of the hydroxyl groups.
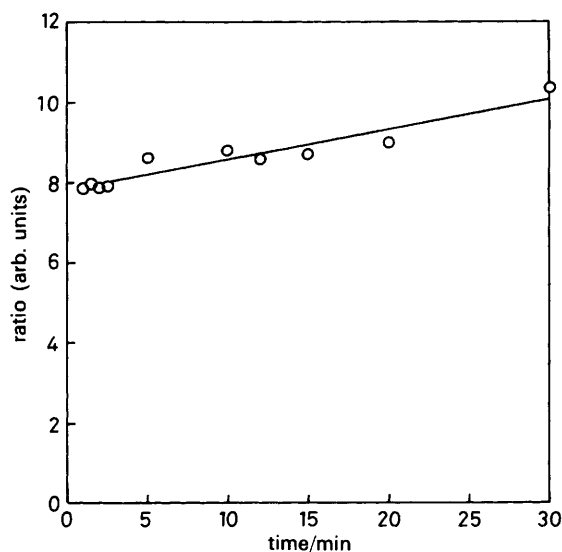
Fig. 3   Ratio of evolved H_2 and the integration of the silane band as a function of reaction time for diborane-treated silica gel
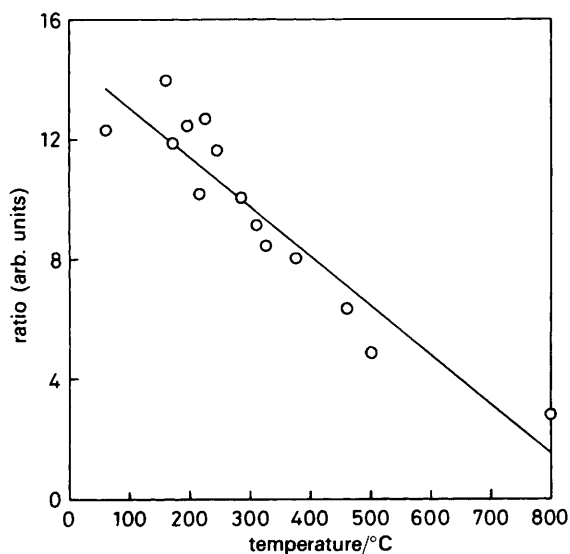

Fig. 4   Ratio of H_2 and the integration of the silane band as a function of the pretreatment temperature of the diborane-treated silica gel

Conclusion

The chemisorption of diborane on the silica gel surface can be re-evaluated owing to the use of FTIR–PAS. Besides the general reaction of borane with surface hydroxyl groups, a competitive side reaction occurs with the siloxane bridges,

resulting in the formation of a silane bond. This side reaction is proposed as follows:
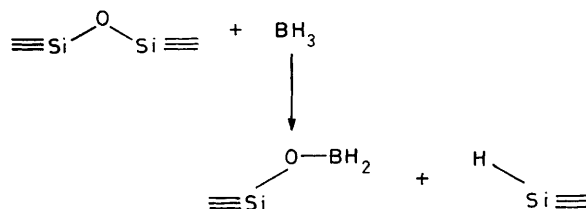
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