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Thermochemistry of hydride and phenyl groups on the surface of amorphous silicon dioxide

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Abstract

The thermodynamic properties of hydride and phenyl groups on the surface of amorphous silicon dioxide are investigated in the presented work. The characteristics of the surface silane centers (≡Si–H) are determined from the data obtained by infrared spectroscopy and caloric measurements. The conversions of hydrogen and benzene with the surface are described by thermodynamic calculations at reactions take place in the gaseous phase.

To model the reaction between hydrogen and the surface the thermodynamic data for $(OH)_{4-n}Si_n$ ($n = 0$–4) in the gaseous phase are used. The surface groups and the model molecules are comparable because the thermodynamic characteristics depend only from the local environment.

The thermodynamic properties of $(OH)_3Si–C_6H_5$ in the gaseous phase are determined to describe the reaction between benzene and the surface. The predications of these calculations are confirmed by the spectroscopic results. The properties of the surface phenyl groups ($≡Si–C_6H_5$) are concluded from these data.

Keywords: Silica surface; Surface group; Surface modification; Infrared spectroscopy; Thermodynamics

1. Introduction

The surface modification of amorphous silicon dioxide has attained increasing technical importance. Complex molecules such as organometallic catalysts and pharmaceuticals are immobilized on the surface [1,2]. The liquid phase is used with priority for the reactions. The problems with the infiltration are avoidable by application of gaseous precursors. The surface modification with gaseous molecules is limited to simple structures but the reactions and the surface groups are thermodynamic describable.

The thermodynamic properties of hydride and phenyl groups on the surface of Aerosil 300 are investigated in the presented work. The surface modification is modeled with help of calculations at reactions take place in the gaseous phase. The comparison with the vapor phase arises from the low group density on the surface. Lateral interactions between the surface groups are negligible [3–5]. The siloxan linkages on the surface are replaced by hydroxyl groups in the gaseous state. The local environment do not change. Thus the surface centers and the molecules in the gaseous state should be comparable. The predications of the calculations are reviewed by experimental data from infrared spectroscopy and thermal analysis on the surface groups.

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2. Experimental

2.1. Information about the adsorbent

Aerosil 300 is a hydrophilic silicic acid and is supplied as a powder by the Degussa AG, Germany. Because of the high specific surface area of ($300 \pm 30\,m^2\,g^{-1}$) the amourphous silicon dioxide is very suitable for analytical measurements. The powder is not porous but the small particles (8 nm diameter) are arranged into agglomerates. Aerosil 300 is of high purity (SiO_2 content > 99.8%) and is made from $SiCl_4$ and H_2/O_2 in a high-temperature hydrolysis process [2].

2.2. Preparation of the modified samples

Before the reaction 10 or 50 mg of the powder is compressed to disks (19 mm diameter) at a pressure of 10^7 Pa. Then the surface modification takes place in a flow reactor. The hydride groups are produced at different temperatures (1123, 1223 and 1323 K) in a stream of hydrogen.

The phenyl groups are made from the hydrogenated samples at 873 K. The benzene is placed in a vaporizer which is temperated at 283 K and vaporized by nitrogen.

The modified disks are suitable for characterization by IR spectroscopy and differential thermal analysis. There is no need for further sample preparations.

2.3. Differential thermal analysis

The differential thermoanalyzer DTA 7 from Perkin-Elmer calibrated in the DSC mode works with synthetic air ($20\,ml\,min^{-1}$). Thermal data of the oxidation are collected in the temperature range of 673–1073 K. Heating rates of 10, 7.5, 5 and $2.5\,K\,min^{-1}$ are used for the measurements.

The sample mass amounts to 15 mg and an unmodified sample is in the comparison crucible.

2.4. IR spectroscopy

The IR spectroscopic measurements take place in transmission with a FTIR spectrometer IFS 48 from Bruker. The resolution of $0.5\,cm^{-1}$ is used for studies of band structures and measurements within the range to $5000\,cm^{-1}$. The disks with a mass of 10 mg have a small thickness. Therefore they are suitable for measurements in the range from 4000 to $400\,cm^{-1}$.

3. Results and discussion

3.1. Thermochemistry of hydride groups on the surface

3.1.1. Reactions in the gaseous phase

The reactions (1)–(4) take place in the gaseous phase. They are in accordance with the hydrogenation of different surface silanol groups. The reaction (1) is a model for the conversion of isolated silanols whereas the reaction (2) takes place on geminal silanol groups. The reactions (3) and (4) are additional conversions which are helpful for the discussion.

$$(OH)_4Si + H_2 \rightleftharpoons (OH)_3SiH + H_2O \tag{1}$$

$$(OH)_4Si + 2H_2 \rightleftharpoons (OH)_2SiH_2 + 2H_2O \tag{2}$$

$$(OH)_4Si + 3H_2 \rightleftharpoons (OH)SiH_3 + 3H_2O \tag{3}$$

$$(OH)_4Si + 4H_2 \rightleftharpoons SiH_4 + 4H_2O \tag{4}$$

With Eqs. (I)–(III) the thermodynamic functions $D_fH(T)$, $D_fS(T)$ and $D_fG(T)$ are calculated from the $C_p(T)$ data for the molecules $(OH)_{4-n}SiH_n$ ($n = 0$–4) [6,7].

$$D_fH(T) = D_fH^{\Theta} + \int_{298}^{T} D_fC_P(T)\,dT \tag{I}$$

$$D_fS(T) = D_fS^{\Theta} + \int_{298}^{T} \frac{D_fC_P(T)}{T}\,dT \tag{II}$$

$$D_fG(T) = D_fH(T) - TD_fS(T) \tag{III}$$

The values for the heat capacities and entropies of H_2 and H_2O at the different temperatures are from the literature [8]. From these data the Gibbs free energy of reaction for the conversions (1)–(4) is plotted in Fig. 1. The thermodynamic equilibrium is on the side of the educts. This is also confirmed by the values of the equilibrium constant at the reaction temperatures usually used in our experiments (Table 1). High temperatures and non-equilibrium conditions are necessary for the formation of Si–H groups. These requirements are given by our experimental conditions. The species

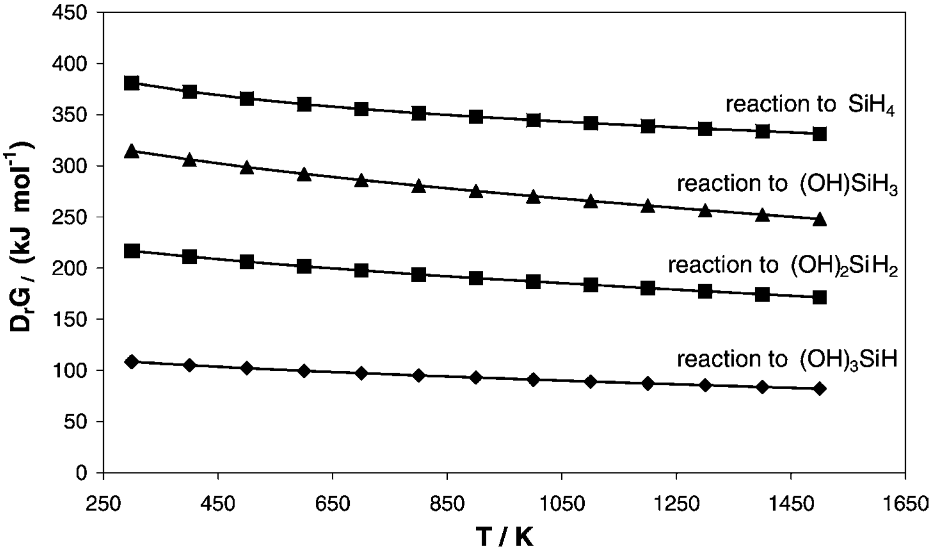

Fig. 1. Gibbs free energy of reaction as function of temperature for the reactions (1)–(4).

$(OH)_3SiH$ is favored. The content of $(OH)_2SiH_2$ is smaller and the formation of $(OH)SiH_3$ or SiH_4 should be nearly excluded.

3.1.2. IR spectroscopy

An IR spectrum of a hydrogenated sample shows different absorption bands of ≡Si–H centers (Fig. 2a). The value of the Si–H stretching vibration is influenced by the number of oxygen bonds (Table 2). The values from Pacchioni and Vitiello are harmonic stretching vibrations calculated from ab initio models [10]. Therefore these values are higher than the experimental ones. The experimental values given in Table 2 are from Fig. 2a–c. The sample was hydrogenated at 1323 K for 5 h. On this condition the species =SiH(OH) is observable. The reasons are structural changes on the surface of Aerosil which run simultaneous to the reaction at the silanol groups.

Table 1
Equilibrium constants K for the reactions (1)–(4) at different reaction temperatures

Reaction	$T = 1123\,K$	$T = 1223\,K$	$T = 1323\,K$
1	7.60×10^{-5}	1.97×10^{-4}	4.39×10^{-4}
2	3.18×10^{-9}	2.13×10^{-8}	1.06×10^{-7}
3	5.05×10^{-13}	7.97×10^{-12}	8.15×10^{-11}
4	1.40×10^{-16}	3.63×10^{-15}	5.65×10^{-14}

According to reaction (5) strained siloxan linkages are broken at higher reaction temperatures.

$$=Si(OH){-}O{-}Si\equiv + H_2 \rightarrow =SiH(OH) + HO{-}Si\equiv \qquad (5)$$

It is difficult to detect the surface species at lower reaction temperatures in spite of the same reaction time. Although =SiH(OH) groups exist on the surface the concentration of $=SiH_2$ centers is small. They are veritably on samples with bigger thickness. The stepwise replacement of two Si–O bonds is identical with the reaction (2) and is not preferred in the light of the thermodynamic statements made for the gaseous phase.

Spectroscopic and thermodynamic properties of the bond between silicon and hydrogen on the surface are experimentally determined by investigations of the first overtone. The first overtone of Si–H centers is covered by combination bands from the silanols. These bands disappear after reaction with vapour of heavy water [4]. The two modes of Fig. 3 are assigned to the both most intensive absorption bands in Fig. 2a. The anharmonic oscillator model is used to characterize the bond between silicon and hydrogen on the surface. With Eqs. (IV) and (V) the data of Table 3 are calculated.

$$\tilde{\nu}_{0-1} = \omega_e - 2\omega_e x_e \qquad \text{(IV)}$$

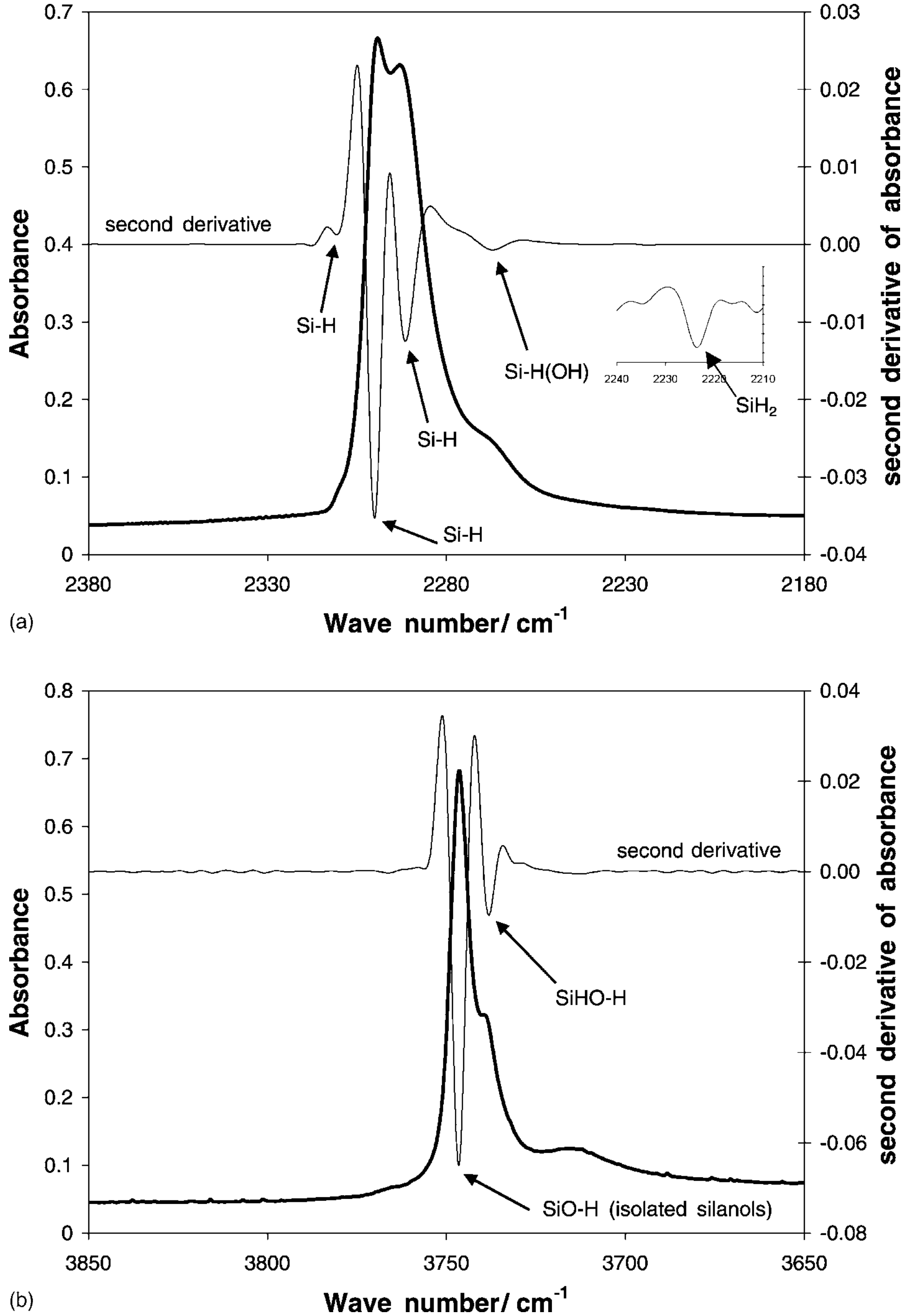

Fig. 2. (a) IR spectrum in the range of absorption of hydride groups. (b) IR spectrum in the range of absorption of silanol groups. (c) Deformation vibration of ≡Si–H groups.

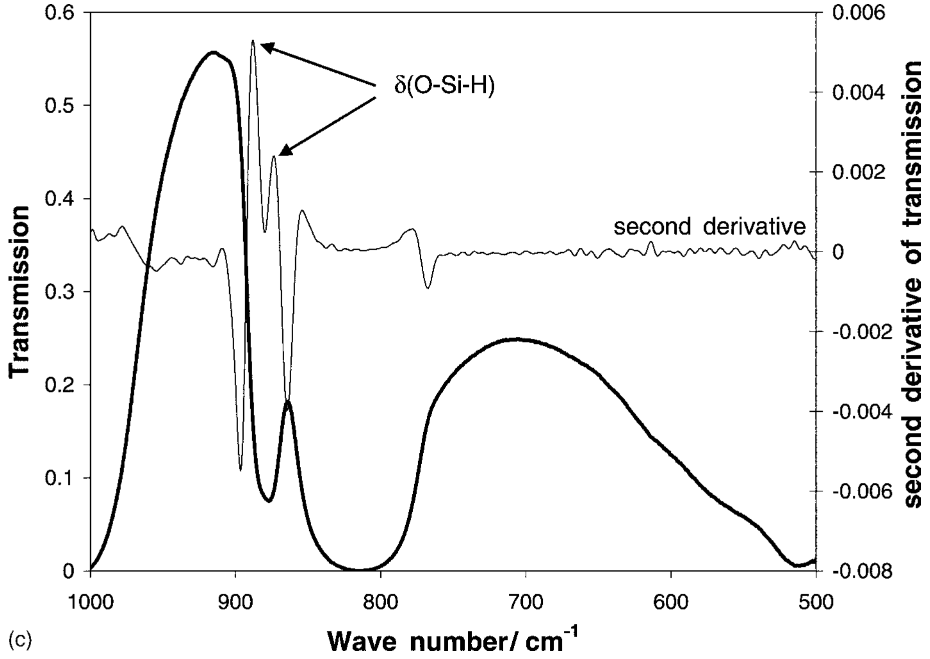

Fig. 2. (*Continued*).

Table 2

Wave numbers of infrared absorption bands of different hydride species on the surface, comparisons with data from the literature

Species	$\tilde{\nu}$ (cm^{-1}; experimental, this work)	Assignment	$\tilde{\nu}$ (cm^{-1}; experimental [9])	$\tilde{\nu}$ (cm^{-1}; ab initio [10])
≡Si–H	2291.5			
	2300.1			
	2310.6	$\tilde{\nu}$(Si–H)	2300	2323
	887.9			
	873.7	δ(O–Si–H)		
=SiH(OH)	2267/3738.2	$\tilde{\nu}$(Si–H)/$\tilde{\nu}$(SiO–H)	2270/3739.4	2308/–
=SiH$_2$	2223.5	$\tilde{\nu}_s$(Si–H)/$\tilde{\nu}_{as}$(Si–H)	2225	2269/2286

$$\tilde{\nu}_{0-2} = 2\omega_e - 6\omega_e x_e \tag{V}$$

where $\tilde{\nu}_{0-1}$ is Si–H stretching vibration, $\tilde{\nu}_{0-2}$ the first overtone of Si–H stretching vibration, ω_e the wave number of harmonic Si–H stretching vibration, x_e the anharmonicity constant.

Table 3

Spectroscopic and thermodynamic characteristics of the ≡Si–H centers on the surface from the two most intensive infrared bands

Parameter		
$\tilde{\nu}_{0-1}$ (cm^{-1})	2291.5	2300.1
$\tilde{\nu}_{0-2}$ (cm^{-1})	4516	4532
ω_e (cm^{-1})	2358.5	2368.3
$\omega_e x_e$ (cm^{-1})	33.5	34.1
E_0 (kJ mol^{-1})	482	478

The binding energy between silicon and hydrogen on the surface is calculated from Eq. (VI).

$$E_0 = \frac{1}{2} hcN_A\omega_e\left(\frac{1}{2x_e} - 1\right) \tag{VI}$$

The binding energies determined by the Birge–Sponer extrapolation are often higher than the values concluded from caloric measurements [11]. The data preparation from [12,13] gives a value of 1.145 for the quotient E_0/D(Si–H). D(Si–H) is the binding energy determined by caloric measurement. The corrected

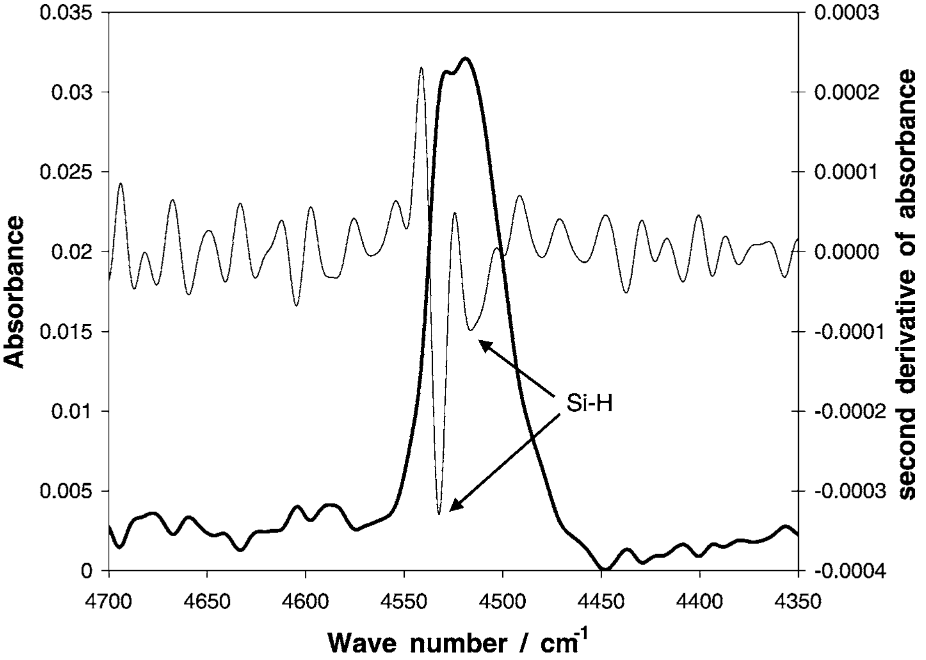

Fig. 3. First overtone of ≡Si–H centers.

values are in very good agreement with the results of other works (Table 4).

The two most intensive absorption bands are assigned to two Si–H modes because the properties of the two modes are nearly equal. In consideration of the theoretical work on silasesquioxanes there are several modes which can assigned to Si–H vibrations [15]. In ordered systems there is almost one mode which is active in the infrared region. Because of the amorphous structure of Aerosil the other modes are also active and a splitting into separate peaks can be observed. This is also valid for the deformation vibration of the ≡Si–H centers. $=SiH_2$ deformations are not detected (Fig. 2c).

Table 4
Bond energy (after correction) of the Si–H bond on the surface, comparisons with data from the literature

Reaction	Value ($kJ\,mol^{-1}$)	Method
$\equiv Si–H \rightarrow \equiv Si^{\bullet} + H^{\bullet}$	421/417	IR (this work)
$\equiv Si–H \rightarrow \equiv Si^{\bullet} + H^{\bullet}$	418 ± 9	Kinetic data (EPR spectroscopy) [14]
$\equiv Si–H \rightarrow \equiv Si^{\bullet} + H^{\bullet}$	440	From D_e, ab initio [10]
$(OH)_3Si–H \rightarrow (OH)_3Si^{\bullet} + H^{\bullet}$	422	Ab initio [6]

3.1.3. *Differential thermal analysis*

According to reactions (6) and (7) the enthalpy of combustion for $(OH)_3Si–H$ and $(OH)_2SiH_2$ is calculated for the gaseous phase at different temperatures (Fig. 4).

$$(OH)_3Si–H_{(g)} + \tfrac{1}{2}O_2 \rightarrow (OH)_4Si_{(g)} \tag{6}$$

$$(OH)_2SiH_{2\,(g)} + O_2 \rightarrow (OH)_4Si_{(g)} \tag{7}$$

The calculated values depend hardly from the temperature. They differ from the result of our caloric measurements. A mean value of $-251\,kJ\,mol^{-1}$ is obtained for the enthalpy of combustion of the hydride groups on the surface. This is the result from our experiments with different surface group concentrations (Fig. 5) [4,5]. Every point in Fig. 5 is a mean value of experiments with different heating rates. The heating rate has no influence on the combustion enthalpy. The experimental value is compared with the calculated data in the gaseous phase (Table 5). The difference come from the condensation of the new formed

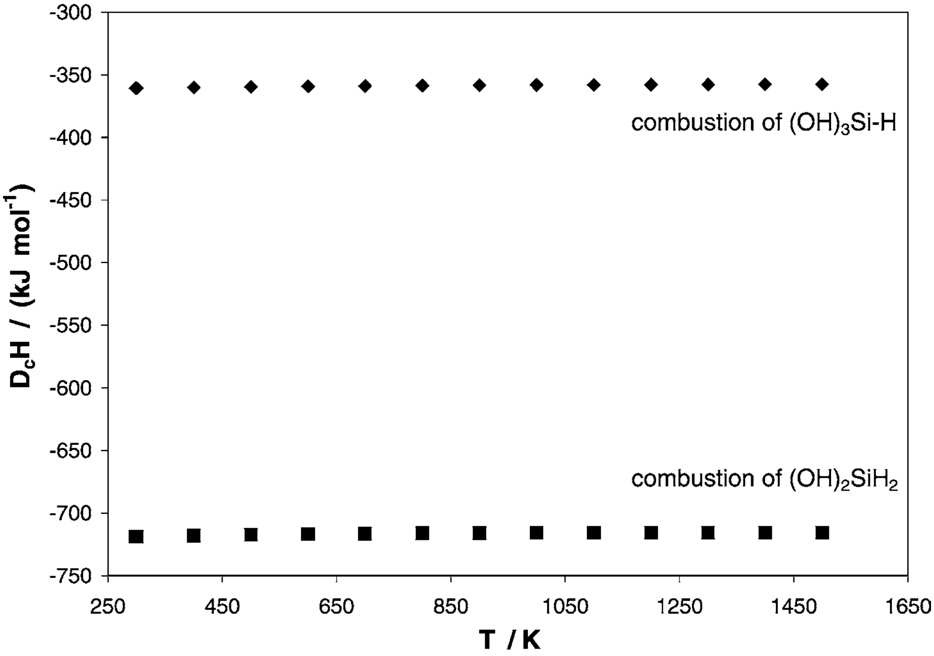

Fig. 4. Combustion of $(OH)_3SiH$ and $(OH)_2SiH_2$ in the gaseous state as function of temperature.

silanols on the surface given by reaction (8) which is not considered in our calculations for the gaseous phase.

$$2{\equiv}\text{Si–OH} \rightarrow {\equiv}\text{Si–O–Si}{\equiv} + H_2O \quad (8)$$

The heat of condensation depends from the distance of the silanols on the surface [16]. Thus a part of the enthalpy of combustion is used. The concentration of $=SiH_2$ centers is negligible. Thus the combustion of

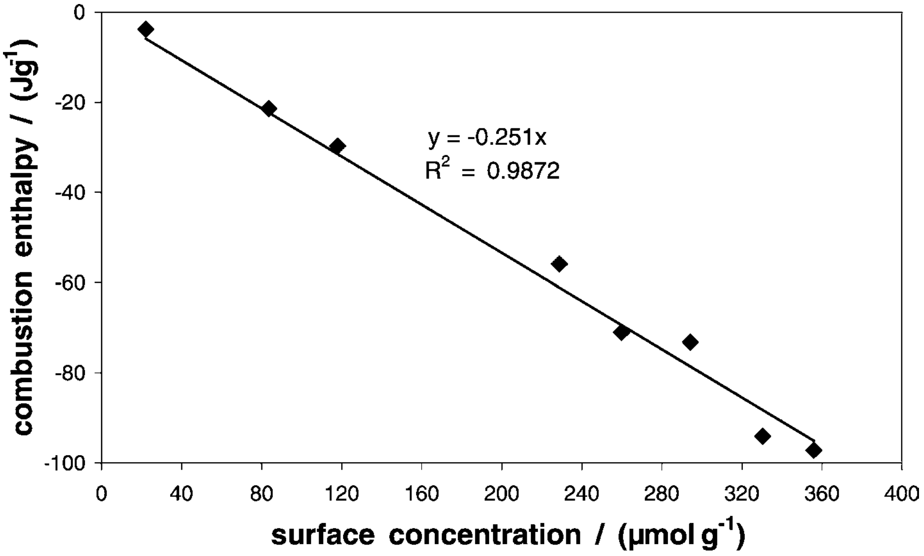

Fig. 5. Combustion enthalpy of hydride groups as function of the surface concentration (both units are related to 1 g Aerosil).

Table 5
Enthalpy of combustion of hydride groups on the surface, comparison with values for the molecules $(OH)_3Si–H$ and $(OH)_2SiH_2$ at 298 K in the gaseous state

Species	D_cH (kJ mol^{-1})
≡Si–H	−251 [4,5]
$(OH)_3Si–H$	−361
$(OH)_2SiH_2$	−719

these surface centers has no influence on the experimental data.

3.2. Thermochemistry of phenyl groups on the surface

The thermodynamic information of ≡Si–H groups are used for a description of the surface modification with benzene. The conversion into $≡Si–C_6H_5$ species is illustrated by reaction (9) takes place in the gaseous phase.

$$(OH)_3Si–H + C_6H_6 \rightleftharpoons (OH)_3Si–C_6H_5 + H_2 \qquad (9)$$

The thermodynamic properties of $(OH)_3Si–C_6H_5$ are necessary to investigate this reaction.

3.2.1. Thermochemistry of $(OH)_3Si–C_6H_5$

According to reaction scheme 1 the enthalpy of combustion at 298 K is calculated for octaphenylcyclotetrasiloxan in the gaseous phase. The necessary data are from the literature [6,8,17]. The combustion leads to $Si(OH)_{4\,(g)}$ because of the formation of new silanols during the oxidation [4,5]. A condensation is not considered.

$[(C_6H_5)_2SiO]_{4\,(s)} + 60O_2 \rightarrow 4SiO_{2\,(s)} + 20H_2O_{(l)} + 48CO_{2\,(g)}$	−26989 kJ mol^{-1}
$[(C_6H_5)_2SiO]_{4\,(g)} \rightarrow [(C_6H_5)_2SiO]_{4\,(s)}$	−148 kJ mol^{-1}
$4SiO_{2\,(s)} + 8H_2O_{(l)} \rightarrow 4Si(OH)_{4\,(g)}$	+675.1 kJ mol^{-1}
$[(C_6H_5)_2SiO]_{4\,(g)} + 60O_2 \rightarrow 4Si(OH)_{4\,(g)} + 12H_2O_{(l)} + 48CO_{2\,(g)}$	−26461.9 kJ mol^{-1}

Reaction Scheme 1.

The enthalpies of combustion for gaseous hexaphenyltrisiloxan and diphenylsilanol at 298 K are given in Table 6. The enthalpy of combustion per phenyl group is calculated from these data. With the mean value the enthalpy of formation for $(OH)_3Si–C_6H_5$ in the gaseous phase is determined according to reaction scheme 2.

Table 6
Enthalpies of combustion for octaphenylcyclotetrasiloxane, hexaphenylcyclotrisiloxane and diphenylsilanol at 298 K in the gaseous state, enthalpy of combustion per phenyl group

Molecule	D_cH^{Θ} (kJ mol^{-1})	D_cH^{Θ} (per phenyl group) (kJ mol^{-1})	∅
$[(C_6H_5)_2SiO]_4$	−26461.9	−3307.7	−3295.7
$[(C_6H_5)_2SiO]_3$	−19886.7	−3314.5	−3295.7
$(C_6H_5)_2Si(OH)_2$	−6529.8	−3264.9	−3295.7

$Si_{(s)} + 2O_2 + 2H_2 \rightarrow Si(OH)_{4\,(g)}$	−1342.3 kJ mol^{-1}
$6C_{(s)} + 6O_2 \rightarrow 6CO_{2\,(g)}$	−2361.1 kJ mol^{-1}
$2H_2 + O_2 \rightarrow 2H_2O_{(l)}$	−571.6 kJ mol^{-1}
$(OH)_4Si_{(g)} + 6CO_{2\,(g)} + 2H_2O_{(l)} \rightarrow (OH)_3Si–C_6H_{5\,(g)} + 15/2O_2$	+3295.7 kJ mol^{-1}
$Si_{(s)} + 3/2O_2 + 4H_2 + 6C_{(s)} \rightarrow (OH)_3Si–C_6H_{5\,(g)}$	$D_fH^{\Theta} = -979.3$ kJ mol^{-1}

Reaction Scheme 2.

This agrees with a value calculated from an increment system ($D_fH^{\Theta} = -947.70$ kJ mol^{-1} [18]).

The binding energies between silicon and substituents X for the molecules $(OH)_3Si–X$ are compared in Table 7. The enthalpy of formation data necessary for the calculation are from the literature

Table 7
Binding energies for the bond between silicon and substituents X in the molecules $(OH)_3Si–X$

Species	D(Si–X) (kJ mol^{-1})
$(OH)_3Si–F$	695
$(OH)_3Si–OH$	604
$(OH)_3Si–Cl$	495
$(OH)_3Si–Br$	429
$(OH)_3Si–CH_3$	433
$(OH)_3Si–C_6H_5$	531

[6,8,18]. The Si–C bond is stronger than the Si–H bond. The Si–C bond in phenylsilantriol is not only a single bond and has parts of a double bond.

The entropy for the molecules X_nSiY_{4-n} ($n = 0$–4) is available by an increment system developed by van Dalen and van den Berg [19]. The molecule is separated in its bonds Si–X and Si–Y. According to Eq. (VII) the entropy of the molecule is calculated from the contributions of its several bonds.

$$S(T) = n\phi(\mathrm{Si}-\mathrm{X})_T + (4-n)\phi(\mathrm{Si}-\mathrm{Y})_T + \tfrac{3}{2}R\ln M - R\ln\sigma \qquad \text{(VII)}$$

where $\Phi(T)$ is contribution to the entropy, R the molar gas constant, M the molecular weight, σ the symmetry constant.

Table 8
Entropy contributions of Si–OH and Si–C_6H_5 increments from 298 to 1500 K

T (K)	$\Phi(\mathrm{Si{-}OH})_T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$\Phi(\mathrm{Si{-}C_6H_5})_T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
298	75.0	149.2
300	75.2	150.2
400	84.8	180.5
500	92.5	210.9
600	98.9	239.1
700	104.5	265.3
800	109.4	290.4
900	113.8	314.4
1000	117.9	335.3
1100	121.7	356.3
1200	125.1	375.1
1300	128.4	393.9
1400	131.4	410.7
1500	134.3	427.4

The contributions of the increments Si–OH and Si–C_6H_5 are calculated from the entropy values of $(OH)_nSiH_{4-n}$ and $Si(C_6H_5)_4$ [6,20]. A compilation of the data is given in Table 8. The entropy for the molecule $(OH)_3Si{-}C_6H_5$ is determined from Eq. (VII). According to the literature a symmetry constant of unity is assumed [19]. Eq. (VIII) is used to calculate the heat capacity from the entropy. The Gaussian least squares method is used to determine the coefficients (Fig. 6).

$$\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_\mathrm{p} = \frac{C_\mathrm{p}}{T} \quad \text{with } C_\mathrm{p} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \qquad \text{(VIII)}$$

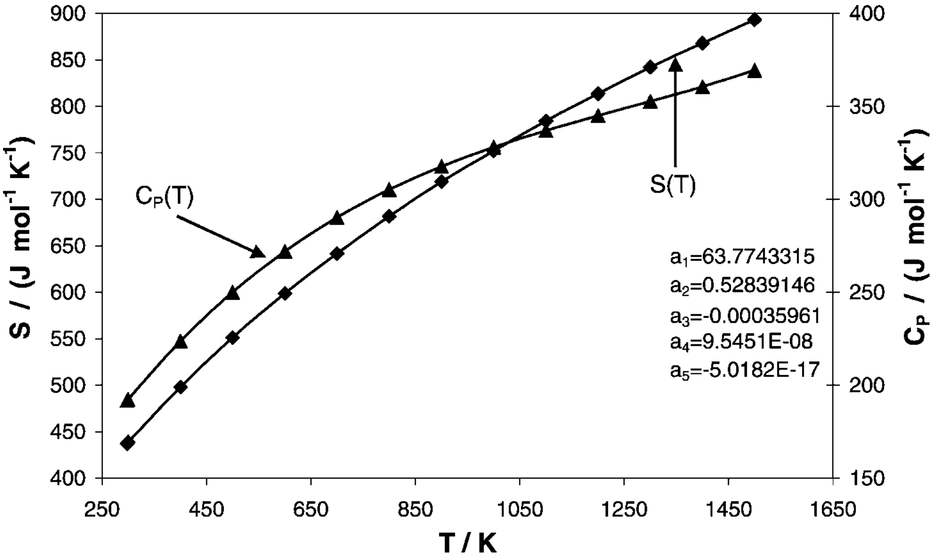

Fig. 6. Entropy and heat capacity of $(OH)_3Si{-}C_6H_5$ as functions of temperature.

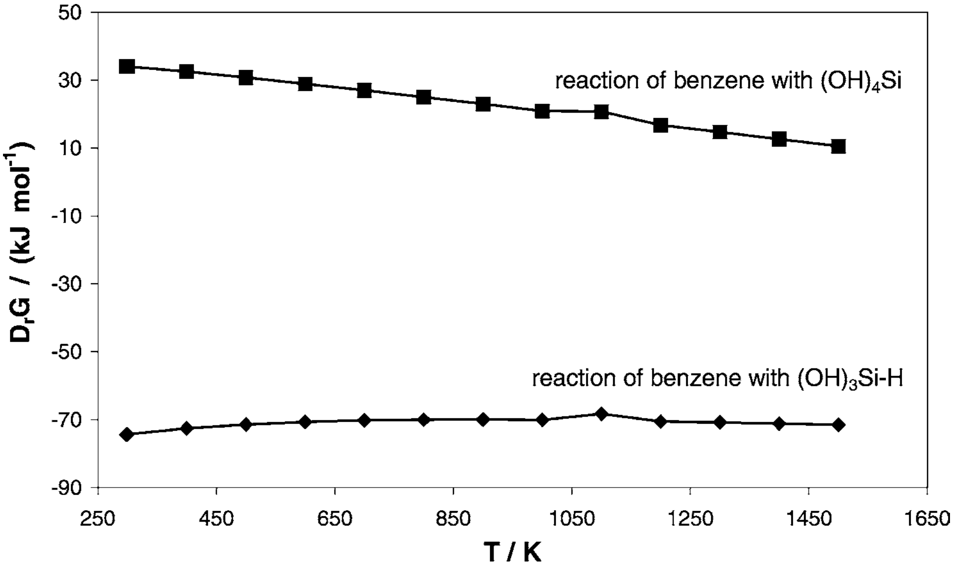

Fig. 7. Gibbs free energy of reaction as function of temperature for reactions (9) and (10).

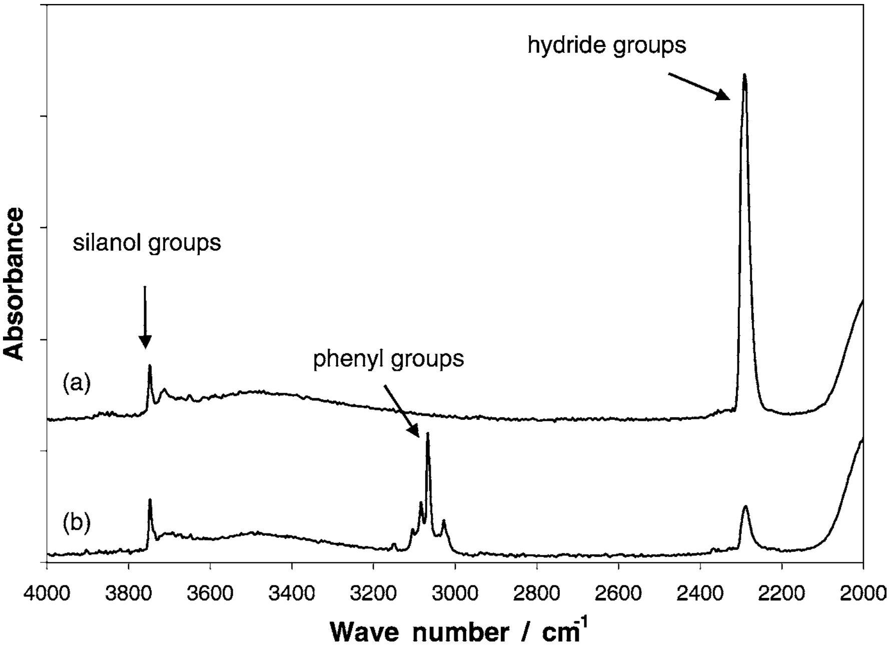

Fig. 8. (a) IR spectrum of a probe with ≡Si–H groups, (b) the same probe after reaction with benzene vapour.

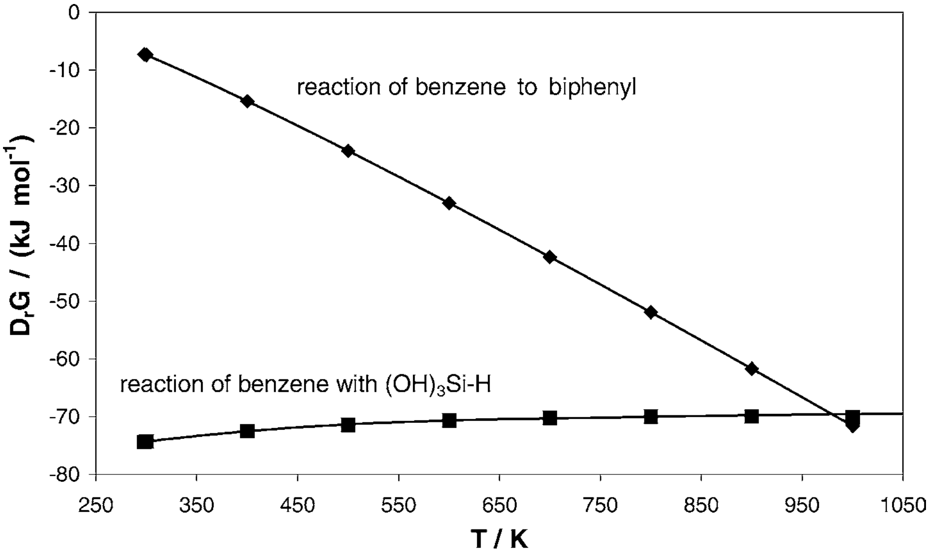

Fig. 9. Gibbs free energy of reaction as function of temperature for reactions (9) and (11).

3.2.2. Comparisons with the experimental data

The Gibbs free energy of reaction for the reactions (9) and (10) is compared in Fig. 7.

$$(OH)_3Si\text{–}OH + C_6H_6 \rightleftharpoons (OH)_3Si\text{–}C_6H_5 + H_2O \qquad (10)$$

The reaction (10) describes the conversion of the silanol groups with benzene. Only for the reaction of $(OH)_3SiH$ the thermodynamic equilibrium is on the side of the reaction products. A reaction temperature of at least 843 K is necessary for the modification because of kinetical reasons. The reaction of $(OH)_4Si$ to phenylsilantriol is excluded. These predictions are confirmed by the experimental results. As can be seen from the two IR spectra in Fig. 8 the silanol groups are not involved in the surface modification with benzene. Only the hydride group concentration gets smaller and phenyl groups arise.

Reaction (11) hinders the modification of hydride groups and induces the condensation of benzene to polyaromatic hydrocarbons.

$$2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2 \qquad (11)$$

The Gibbs free energy of reaction for the reactions (9) and (11) is compared in Fig. 9. The thermodynamic data of biphenyl are from the literature [8,21]. The reaction of benzene to biphenyl becomes significant at a temperature of 933 K because of kinetical reasons. Above this temperature biphenyl is identified on the surface by NMR measurements [22]. The two curves in Fig. 9 cross at a temperature of 979 K. Above this temperature the formation of biphenyl becomes dominant.

4. Conclusions

The reactions of hydrogen and benzene with the surface of amorphous silicon dioxide are characterized with the help of model reactions take place in the gaseous phase. The data obtained by infrared and thermal measurements document the predications of the calculations.

At high temperatures the reaction of hydrogen with the surface of amorphous silicon dioxide results preferably in Si–H groups. This is in accordance with the thermodynamic statements obtained for the gaseous state and add previous results [4,5].

The Si–H bond is investigated by infrared measurements. The binding energy between silicon and hydrogen on the surface agrees with the value obtained in the gaseous phase. This energy is smaller than in other molecules of the type $(OH)_3Si\text{–}X$. Thus the hydride groups on the surface are a starting point for following reactions. This is discussed on the example of the reaction with benzene. With the information available from the literature the thermodynamic properties of phenylsilanetriol are determined. The predictions calculated for the gaseous state are confirmed by the spectroscopic results.

There are similarities between the thermodynamic properties in the gaseous phase and on the surface. The thermodynamic characteristics depend only from the local environment.

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