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ORIGINAL CONTRIBUTION

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The versatile surface properties of poly(cyclopentadiene)-modified silica particles (PCPD–silica): XPS and electrokinetic studies

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We dedicate this article to the 60th birthday of Professor Günter Marx, Technical University of Chemnitz

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Abstract Surface properties of poly(cyclopentadiene)–silica hybrid particles (PCPD–silica) were studied by means of XPS and electrokinetic measurements. The surfaces of PCPD–silica particles exhibit two different areas with different properties: bare silica holes and PCPD patches. The PCPD chains contain different functional groups such as alcohol and carbonyl groups that were identified by XPS. The PCPD chains are grafted covalently onto the silica surface via Si–O–C bonds created by the reaction of silanol groups and active PCPD chains. The amount of Si–O–C was examinated by means of XPS.

The Brønsted acidity of the residual silanol groups was determined by means of electrokinetic measurements. It was found that the pK_a values of the residual silanol groups increase with increasing polymer content on the particle surface.

The surface acceptor strengths of the hybrid particles in non-aqueous liquids were investigated by the solvatochromic indicator bis(1,10-phenanthroline)-cis-dicyano-iron-II in 1,2-dichloroethane.

Key words Polymer–silica hybrid materials – cationic surface polymerization – poly(cyclopentadiene) – X-ray photoelectron spectroscopy – particle electrophoresis – solvatochromic measurements – acid-base properties

Introduction

During the last years several procedures have been developed to produce novel synthetic polymer–inorganic oxide hybrid materials [1–4]. The advanced properties of such new materials are mainly determined by the structure formation between the participating components and the controlled surface reactivity [5].

One of the synthetic methods to obtain novel polymer–silica hybrid particles is cationic surface polymerization [6–8]. Normally, the combination of silica and soluble polymers obtained by common cationic polymerization would be a system of low reactivity. However, it has been shown that cationic surface polymerization of cyclopentadiene (CPD) onto silica particles is a powerful tool to obtain new materials with advanced properties [9–11].

Cationic polymerization of CPD on the surface of silica particles yields coated silica particles and small amounts of soluble oligomers with very broad molecular weight distribution [6, 7]. The degree of coating can be simply controlled by the concentrations of the CPD monomer, the nature and concentration of the initiator, and the reaction temperature [6]. Thus, it is possible to synthesize functionalized PCPD–silica particles with different surface coverages PCPD ranging from 1 to 20% [6].

Mechanistic aspects of the structure formation of PCPD on the silica particle surface were investigated by solution state ^{1}H-NMR, solid state ^{13}C{^{1}H}-CP-MAS-NMR, and UV/VIS spectroscopy during polymerization

[7]. The formation of covalent Si–O–C-bonds was inferred by the $^{13}C\{^{1}H\}$-CP-MAS-NMR results [7].

A typical IR spectrum of PCPD–silica shows that the residual silanol groups can be identified by the small peak at $\tilde{\nu} = 3740\,\mathrm{cm}^{-1}$ (free silanol groups) and the broad signal near $\tilde{\nu} \approx 3400\,\mathrm{cm}^{-1}$ (coordinated silanol groups). Characteristic absorption bands of the PCPD layer were also found in the IR spectrum [6–8].

Therefore, it is assumed that the composite particles bear two different areas with quite different properties (Fig. 1):

(i) The bare silica part (white areas in Fig. 1) is acidic and polar, but its polarizability is low. Polarity and donor acceptor parameters of commercially available silica have been reported by the authors recently [9].

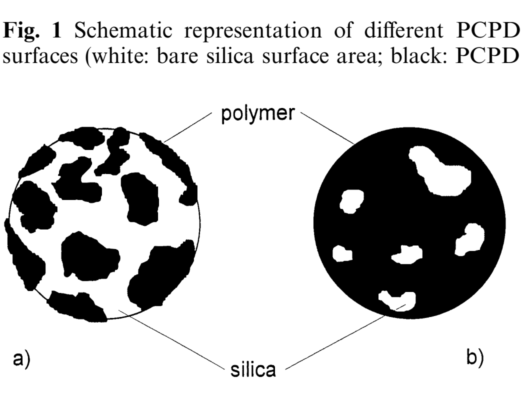
(ii) The PCPD-layer (black areas in Fig. 1) is weakly polar but its polarizability is relatively high, and therefore the ionization potential of the PCPD-patches is relatively low ($I_p = 8.1 \pm 0.2$ eV) [7].

Depending on the degree of coating the hybrid particle surface may be regarded as a bare silica surface with PCPD patches or a PCPD surface with silica patches (compare Fig. 1a and b) [6].

The stepwise covering of the silica surface by PCPD chains lead us to expect that the hybrid particle surface may change from polar to non-polar. Detailed knowledge of the surface properties of the hybrid materials is important for their further applications, as fillers in plastics, as stationary chromatographic phases, or as adsorbents for different organic molecules. The objective of this paper is to investigate the versatile surface properties of PCPD–silica.

X-ray photoelectron spectroscopy (XPS), particle electrophoresis in aqueous solutions, and solvatochromic measurements were applied to obtain information on the nature of the hybrid surface and the interphase between silica and the PCPD layer. XPS should give information of the molecular architecture of the bare and modified silica surface. The Brønsted acid–base behavior was described quantitatively by modeling the results of electrophoresis according to an improved electrochemical double layer model [8, 9]. The Lewis acid properties of PCPD–silica particles were investigated in 1,2-dichloroethane by means of the solvatochromic dye bis(1,10-phenanthroline)-cis-dicyano-iron-II [Fe(phen)$_2$(CN)$_2$] as a surface polarity indicator [9, 14].

Fig. 1 Schematic representation of different PCPD coated silica surfaces (white: bare silica surface area; black: PCPD layer)



Experimental part

PCPD–silica hybrid particles

The experimental procedure for the cationic coating polymerization of cyclopentadiene on silica is reported in detail in Ref. [6]. For experiments in this paper triphenylmethyl bromide as well as trifluoroacetic acid were used as initiators for the polymerization of cyclopentadiene in the presence of dried silica suspended in 1,2-dichloroethane. The PCPD–silica particles were neutralized after the coating polymerization. The unrefined particles were washed several times with methanol and acetone and dried in vacuum. The colour of those PCPD–silica particles is yellow or orange, depending on the degree of coating. The degree of coating was examined by combustion analysis in terms of carbon percent weight (w/w% C) according to [6]. The abbreviation PCPD(y)–silica used below means the carbon content of the particle, where y is the w/w% of carbon.

X-ray photoelectron spectroscopy

A KRATOS ES 300 spectrometer was used to acquire photoelectron spectra of pure and modified silica powder surfaces. Unmonochromatized Mg $K\alpha_{1,2}$ radiation was used as the excitation source.

The binding energy (BE) scale of the spectrometer was set on the Cu $2p_{3/2}$ peak at BE = 932.67 eV and the Au $4f_{7/2}$ peak at BE = 84.00 eV.

Data accumulation and component peak analysis were performed on an IBM PC. The Gaussian component peaks were fitted by the peak maximum position, the full-width at half-maximum and the peak area. To compensate the electrical charging during the measurements all binding energies were adjusted to the hydrocarbon component ($-C_xH_y-$) at BE = 285.00 eV [15].

To identify alcoholic groups in the PCPD–silica surface region labeling reactions were carried out as solid–gas phase reactions [16]. For that purpose, a dried and degassed sample was introduced in a clean atmosphere of trifluoroacetic anhydride where the labeling reaction took place. After 4 h, the surplus of trifluoroacetic anhydride was removed. Then the sample was transferred to the analysis chamber of the photoelectron spectrometer.

Electrokinetic measurements

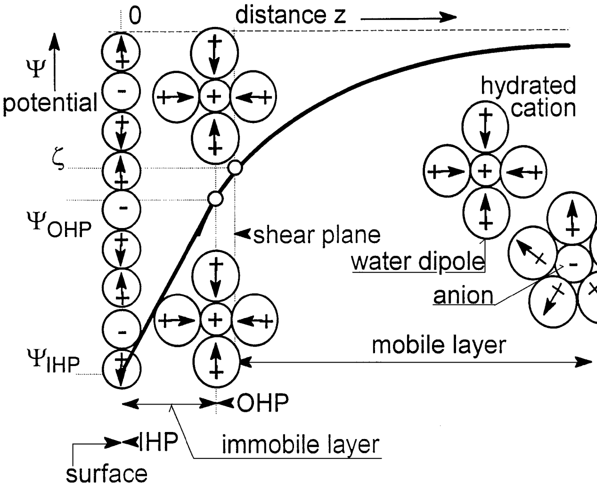
Theory

Electrokinetic phenomena may be observed in systems where a charged solid moves tangentially with respect to a liquid. To reach chemical equilibration between the two phases functional groups of the solid surface can undergo dissociation reactions or specific ion adsorption may take place. The charges on the solid surface are compensated by the adsorption of oppositely charged ions plus negative adsorption of co-ions. An electrochemical double layer showing a surplus of charge carriers is built-up (Fig. 2) [17]. The surplus of charges at the surface generates an electrical potential between the solid and the liquid phase (Fig. 2).

It is important to note, that the driving force for the build-up of the electrochemical double layer is the result of the chemical equilibrium between the two phases. From this point of view, it is possible to describe the thermodynamic behavior of a solid surface by its contact with different aqueous electrolyte solutions [18, 19].

A measure of the electrochemical double layer is the electrokinetic potential (zeta potential). It can be determined experimentally by applying an external force to induce a relative motion of the solid and liquid phase. During the motion of the liquid phase a part of the electrochemical double layer sticks to the solid surface, while the other part is sheared and moved with the liquid (Fig. 2). The electrical potential at the shear plane is called zeta potential (ζ).

Fig. 2 Build-up of the electrochemical double layer according to the Gouy–Chapman–Stern–Grahame model [17]



A detailed overview about the different experimental methods to examine the zeta potential is given by Jacobasch et al. [20].

According to the well-established Gouy–Chapman–Stern–Graham model (Fig. 2) the electrochemical double layer is divided into three parts [17]. In the inner Helmholtz plane (IHP) the adsorbed charge carriers, which have lost fully or partially their hydration sheath are strongly fixed on the solid surface. The ions in the outer Helmholtz plane are charged oppositely to the IHP charge, and did not lose their hydration shell. They are also strongly fixed via Coloumb forces. The remaining surplus of charges is compensated by ions in the diffuse layer.

The condition of charge neutrality requires that the sum of the charge densities σ in the three layers must be zero (Eq. (1)).

$$\sigma^{\mathrm{IHP}} + \sigma^{\mathrm{OHP}} + \sigma^{\mathrm{diffuse}} = 0 \ . \tag{1}$$

In the case of an 1 : 1 electrolyte the charge density in the diffuse layer can be described by means of the Gouy–Chapman approach (Eq. (2)) [19, 21].

$$\sigma^{\mathrm{diffuse}} = \sqrt{8 \cdot RTc^{\infty}\varepsilon_{\mathrm{r}}\varepsilon_0}\,\sinh\left[\frac{F\zeta}{2RT}\right] , \tag{3}$$

where T is the absolute temperature, R is the gas constant, F is the Faraday constant, c^{∞} is the electrolyte concentration in the liquid bulk phase, ε_0 is the permittivity of the free space, and ε_{r} is the permittivity of the liquid.

The charge densities in the inner and outer Helmholtz planes are given by the number of excess ions (Eqs. (3) and (4)) [12]. In the case of silica H^+ and OH^- are the potential-determining ions that were adsorbed in the IHP, while the inert electrolyte ions (K^+ and X^-) are adsorbed in the OHP and in the diffuse part of the double layer [17, 21].

$$\sigma^{\mathrm{IHP}} = (x^{\mathrm{IHP}}_{\mathrm{H^+}} - x^{\mathrm{IHP}}_{\mathrm{OH^-}})e_0N \ , \tag{3}$$

$$\sigma^{\mathrm{OHP}} = (x^{\mathrm{OHP}}_{\mathrm{K^+}} - x^{\mathrm{OHP}}_{\mathrm{X^-}})e_0N \ , \tag{4}$$

where e_0 is the elementary charge, N is the number of the total number of adsorption sites, and x^k_i is the molar fraction of the ionic species i in the k plane.

The charge distribution in the IHP and OHP can be expressed by the Boltzmann approach. According to Stern [21] the specific adsorption molar free energy Φ_i of the ion species i onto a non-charged solid surface has to be introduced in the Boltzmann approach (Eq. (7)).

$$c_i^k = c_i^\infty \exp\left[-\frac{\upsilon_i F \Psi^k - \Phi_i}{RT} \right] , \tag{5}$$

where Ψ^k is the potential in the k plane, υ_i is the stoichiometric number which is positive for cations and negative for anions, c_i^k is the concentration of the ionic species i in the k plane.

For our model we will assume, that Ψ^{OHP} is approximately equal to ζ. With that assumption Eqs. (4) and (5) give Eq. (6), while from Eqs. (3) and (5), Eq. (7) follows:

$$\frac{\sigma^{\mathrm{OHP}}}{e_0 N} = \frac{c_{\mathrm{H^+}}^\infty \exp[-(F\zeta - \Phi_{\mathrm{H^+}})/RT] - c_{\mathrm{OH^-}}^\infty \exp[(F\zeta - \Phi_{\mathrm{OH^-}})/RT]}{c_{\mathrm{H^+}}^\infty \exp[-(F\zeta - \Phi_{\mathrm{H^+}})/RT] + c_{\mathrm{OH^-}}^\infty \exp[(F\zeta - \Phi_{\mathrm{OH^-}})/RT] + 55.5\,\mathrm{mol\,l^{-1}}} , \tag{6}$$

$$\frac{\sigma^{\mathrm{IHP}}}{e_0 N} = \frac{-c_{\mathrm{X^-}}^\infty \exp[(F\Psi^{\mathrm{IHP}} - \Phi_{\mathrm{X^-}})/RT] + c_{\mathrm{K^+}}^\infty \exp[-(F\Psi^{\mathrm{IHP}} - \Phi_{\mathrm{K^+}})/RT]}{c_{\mathrm{X^-}}^\infty \exp[(F\Psi^{\mathrm{IHP}} - \Phi_{\mathrm{X^-}})/RT] + c_{\mathrm{K^+}}^\infty \exp[-(F\Psi^{\mathrm{IHP}} - \Phi_{\mathrm{K^+}})/RT] + 55.5\,\mathrm{mol\,l^{-1}}} , \tag{7}$$

The capacity C^{HP} of the layer between the two Helmoltz planes can be calculated as follows [13]:

$$C^{\mathrm{HP}} = \frac{\sigma^{\mathrm{IHP}} - \sigma^{\mathrm{diffuse}}}{\zeta - \Psi^{\mathrm{IHP}}} . \tag{8}$$

Equations (1), (3), (4) and (6)–(8) contain six parameters: the adsorption molar free energies of ionic species $\Phi_{\mathrm{K^+}}$, $\Phi_{\mathrm{X^-}}$, $\Phi_{\mathrm{H^+}}$, and $\Phi_{\mathrm{OH^+}}$,the capacity C^{HP}, and the charge density $\sigma^{\mathrm{diffuse}}$. To determine the six parameters the set of equations can be solved with the measured function $\zeta = \zeta(\mathrm{pH}, c^\infty)$ as input values [13]. With the adsorption molar free energies $\Phi_{\mathrm{H^+}}$, and $\Phi_{\mathrm{OH^-}}$ pK_a and pK_b can be determined (Eqs. (9) and (10)) [22]. These values are parameters to describe the Brønsted acidicity and basicity, respectively,

$$\exp\left[-\frac{\Phi_{\mathrm{OH^-}}}{RT} \right] = \frac{10^{-\mathrm{p}K_a} \cdot x_{\mathrm{H_2O}}}{K_w} , \tag{9}$$

$$\exp\left[-\frac{\Phi_{\mathrm{H^+}}}{RT} \right] = \frac{10^{-\mathrm{p}K_b} \cdot x_{\mathrm{H_2O}}}{K_w} , \tag{10}$$

where K_w is the ion product of water, and $x_{\mathrm{H_2O}}$ is the molar fraction of water in electrolyte solution. The zeta potential values measured in dependence on varied pH of the liquid phase were used to determine the Brønsted acid–base properties of the solid surfaces.

Experimental

The electrokinetic measurements of PCPD–silica were carried out as particle microelectrophoresis experiments by means of a Repap-Zeta-Potential-Meter. For each measuring point 0.05 g of a sample were suspended in 25 ml of a 0.001 mol l^{-1} aqueous KCl solution. The pH value of the suspension was changed by adding HCl or KOH. The chemical equilibrium of the suspension was reached after shaken weakly for 24 h. Then, the suspension was poured into the measuring cell equipped with two platinum electrodes. Before the first measurement was started the pH value was measured. During all measurements the external electrical field strength applied on the measuring cell was $\mathbf{E} = 14.6\,\mathrm{V\,cm^{-1}}$. Under this condition the particles moved slowly through the measuring cell. The individual electrophoretic velocity of about 50 particles was determined from distance and time measurements in the two opposite directions $\mathbf{v}_1$ and $\mathbf{v}_2$. From the average velocity $\bar{\mathrm{v}}$ the zeta potential value (ζ) was calculated by means of the simple Smoluchowski equation [23, 24] (Eq. (11)). Although the Smoluchowski equation does not reflect the surface conductivity, it has been used widely for semiquantitative interpretation of electrokinetic measurements.

$$\zeta = \frac{\bar{\mathrm{v}} \cdot \eta}{\mathbf{E} \cdot \varepsilon_0 \cdot \varepsilon_r} , \tag{11}$$

where η is the viscosity of the liquid.

Solvatochromic measurements

Solvatochromic measurements were carried out with the probe molecule bis(1,10-phenanthroline)-cis-dicyano-iron-II [Fe(phen)$_2$(CN)$_2$] dissolved in 1,2-dichloroethane. First, PCPD–silica particles were suspended in the blue-colored solution of Fe(phen)$_2$(CN)$_2$ until the absorption intensity at $\tilde{\nu} = 16\,300\,\mathrm{cm^{-1}}$ in the supernatant solution was constant. Then, the colored PCPD–silica particles were filtered and dried in vacuum. Vis-measurements at the loaded particles were carried out employing a Specord M 40 spectrometer (Carl Zeiss Jena) equipped with a special device for recording the reflectance spectra.

Results and discussion

X-ray photoelectron spectroscopy

In the surface region of PCPD–silica hybrids carbon, oxygen, and silicon were detected. The surface region of bare silica dried at 200 °C under vacuum conditions contains no carbon impurities. No traces of fluorine were found in hybrid materials where trifluoroacetic acid was used as initiator for the cationic polymerization.

Figure 3 shows a typical C 1s spectrum of a PCPD–silica composite. The C 1s peak showed a shoulder at higher binding energies (BE) which suggest the presence of carbon–oxygen bonds. Therefore, the peak was decomposed into three constituents. Component peak **A** at BE = 285.0 eV represents carbon–carbon and carbon–hydrogen bonds, which are expected for PCPD. Component peak **B**, appearing at 286.65 eV, is significant for alcohol and ether groups. **C**, at BE = 288.2 eV, reflects the presence of carbonyl groups. Functional groups containing oxygen may be introduced in the PCPD molecule by autoxidation [25].

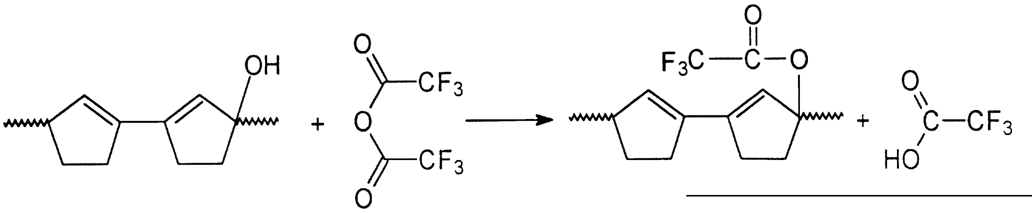
To prove the presence of alcohol groups, the PCPD–silica composites were labelled with trifluoroacetic acid anhydride in a gaseous phase reaction according to Everhart and Reilley [16]. Accessible –OH groups react with the agent and yield trifluoroacetic acid esters (Eq. (12)).

The introduced fluorine can be detected in the XPS spectrum at BE = 688.63 eV. Thus, in the C 1s spectrum of the labelled hybrids two new component peaks appear (Fig. 4). They represent the CF_3 (**E**) and the ester group (**D**). The peak area of one of the two new component peaks is a measure of the number of alcoholic –OH groups (grey area in Fig. 4). However, a quantitative examination does not seem possible because the ratio of the whole number of –OH groups to that of the accessible number of –OH groups is not quite clear.

In contrast to the alcoholic –OH groups in the PCPD chain the SiOH groups at the silica surface are acidic and do not undergo ester formation with trifluoroacetic acid anhydride. Treatment of bare silica with trifluoroacetic acid anhydride in gaseous atmosphere did not introduce fluorine in the sample surface.

The high-resolution Si 2p spectrum of PCPD–silica can be decomposed into two component peaks, while the spectrum of bare silica shows only a single peak at BE = 103.5 eV (**H**) (Fig. 5).

This binding energy at 103.5 eV is typical for $\underline{\mathrm{Si}}$–O bonds of SiO_2 surfaces [26–28]. The second component peak (**G**) in the Si 2p spectrum of PCPD–silica is shifted by



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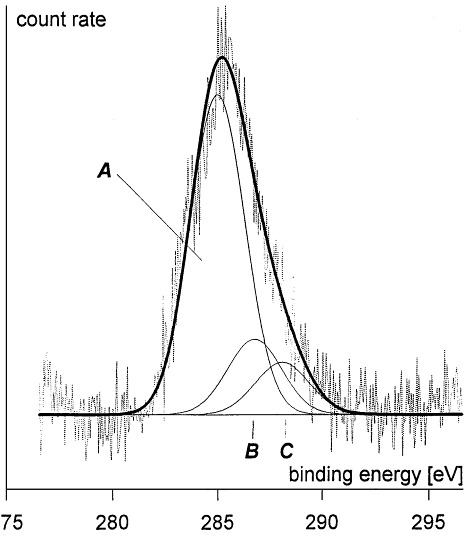


Fig. 3 High-resolution C 1s spectrum of PCPD(12.5)–silica

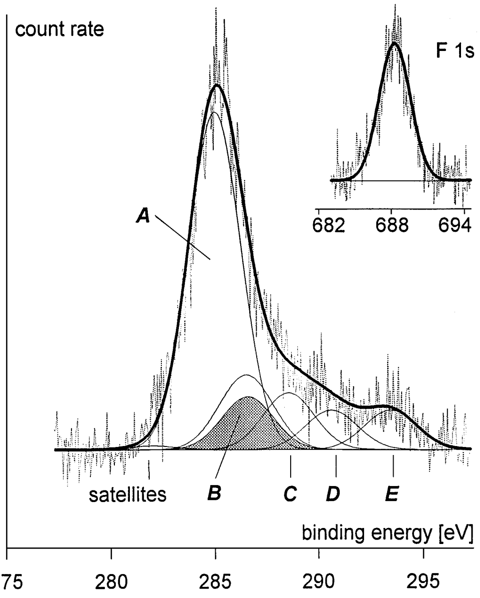
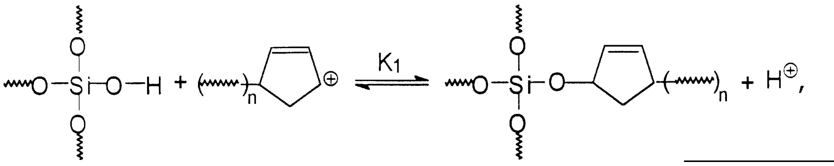


Fig. 4 High-resolution C 1s spectrum of PCPD(12.5)–silica after labeling with trifluoroacetic acid anhydride (gray: amount of alcohol groups labeled with trifluoro acetic anhydride)

approximately 1.5 eV to a lower binding energy. That peak position may indicate the presence of covalent Si–O–C bonds between silica and PCPD.

Figure 6 shows that the relative peak area of the component peak **G** depends on the initial ratio of CPD and initiator. Increasing the initial content of CPD increases the number of occupied SiOH groups. On the other hand, an increase of the number of initiator molecules does not increase the number of Si–O–C bonds. These results point to a catalytic effect of the initiator to yield Si–O–C bonds. It can also be concluded that only a certain number of silanol groups are able to ionize the initiator molecules that act as a nucleation centre to start PCPD chains. These active chains react with silanol groups to form Si–O–C bonds and protons. The latter can initiate the formation of further cyclopentadienium cations (Eqs. (13) and (14)). These chains obtained by silanol-mediated transfer can act in the same way (Eq. (13)). The "surface-mediated transfer to the monomer reaction" helps to explain that the amount of Si–O–C bonds correlates with the monomer and not with the initiator concentration.



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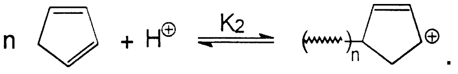


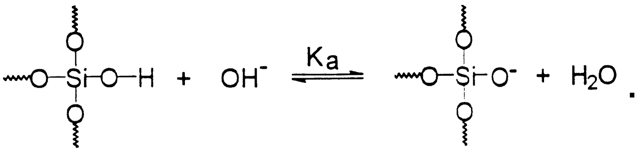
(14)

The formation of covalent Si–O–C bonds was also evidenced by solid state $^{13}C\{^1H\}$–CP–MAS–NMR spectroscopy [6]. Obviouslsy, XPS is a successful completing method to give information on the quantity of Si–O–C bonds, which is impossible by the CP–MAS–NMR method employed.

Electrokinetic measurements

Figure 7 shows the dependencies of the zeta potential on the pH of differently concentrated aqueous KCl solutions for the bare silica surface.

The functions $\zeta = \zeta(\mathrm{pH}, c^{\infty})$ are characteristic for surfaces containing pH-dependent dissociable surface groups. In the presence of the Brønsted base OH^-, the Brønsted acidic SiOH groups undergo dissociation reaction according to Eq. (15).



(15)

Negatively charged silanol ions on the surface lead to negative zeta potential values. With increasing pH of the solution the dissociation reaction proceeds on the bare silica surface. Therefore, the number of negative surface charges increases and the zeta potential values decrease. After complete dissociation of all dissociable silanol groups the zeta potential values remain constant with further increasing pH values.

The isoelectric point of the bare silica surface has been determined to be approximately IEP = 2.1. From the independence of the isoelectric point of the electrolyte concentration it can be concluded that only hydroxide (OH^-) and hydronium (H_3O^+) ions determine the surface potential. This means that specific adsorption of the electrolyte ions K^+ and Cl^- does not take place.

According to Boltzmann's equation the concentration of each ion species i in the shear plane of the electrochemical double layer may be described by Eq. (16).

$$c_i^{\zeta} = c_i^{\infty} \exp\left[-\frac{F\zeta}{RT}\right]. \tag{16}$$

In case $\zeta = 0$ the bulk concentration c_i^{∞} equals the concentration in the shear plane c_i^{ζ}. Eq. (16) shows for the potential-determining OH^- ions that at $\zeta = 0$ the pH value of the bulk phase is equal to the pH value in the shear plane.

PCPD grafted onto the silica surface changes characteristically the electrokinetic behavior as a function of the pH strength of the aqueous electrolyte solution (Fig. 8).

At low pH values (pH < 5) the shapes of the $\zeta = \zeta(\mathrm{pH})$ graphs are similar to that for bare silica. However, plateau regions were not observed. In the high pH-region, the zeta

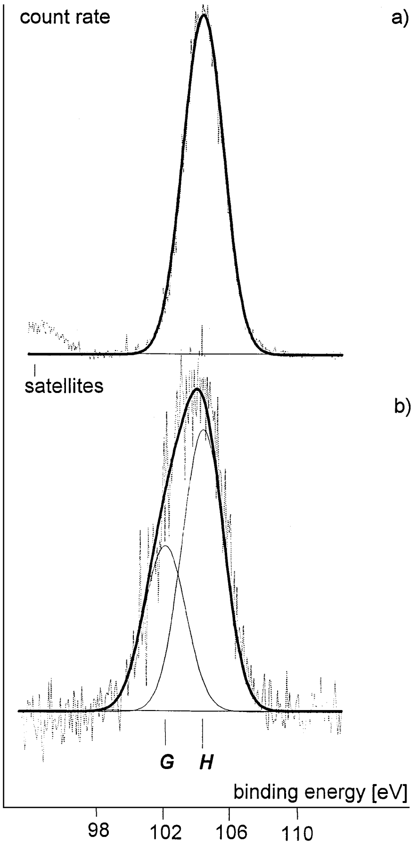


Fig. 5 High-resolution Si 2p spectra of bare silica (a) and PCPD(12.5)–silica (b)

potential amounts continues to increase with increasing pH. Obviously, adsorption of OH^- ions occurs at $pH > 5$, while in the lower pH range residual silanol groups undergo dissociation reactions.

Typical sites for the adsorption of OH^- ions are hydrophobic surface centres [29]. Therefore, an increase of the amount of hydrophobic PCPD patches on the hybrid particle surface influence the slope of the function $\zeta = \zeta(\mathrm{pH})$. That means, the linear functions $\zeta = \zeta(\mathrm{pH})$ at $pH > 6$ show Freundlich isotherms describing the adsorption equilibration of OH^- ions on the PCPD patches. Figure 9 shows that the slope $|d\zeta/d(\mathrm{pH})|$ at $pH > 6$ depends linearly on the polymer content of the hybrid particle surface. Althrough the Freundlich isotherm cannot be interpreted quantitatively increased adsorption free energy of OH^- ions with increased slope $|d\zeta/d(\mathrm{pH})|$ can be concluded from Fig. 9. Obviously, an increased amount of PCPD patches on the hybrid surface allows an enhanced adsorption of OH^- ions with increasing the pH of the aqueous solution. The adsorption of OH^- ions leads to an increased negative charge density which increases the zeta potential.

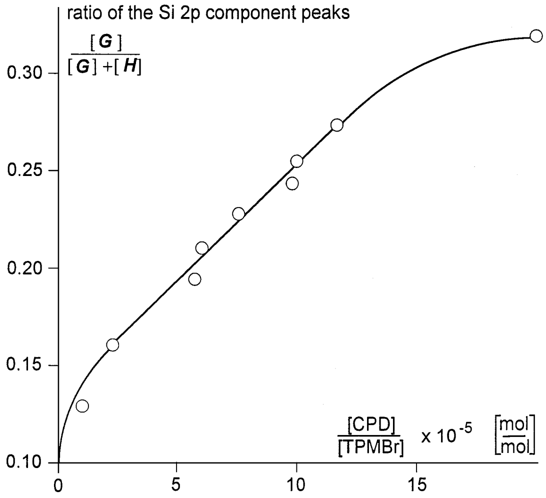


Fig. 6 Amount of Si–O–C bonds as function of the initial ratio of CPD and triphenylmethyl bromide (CPD TPMB)

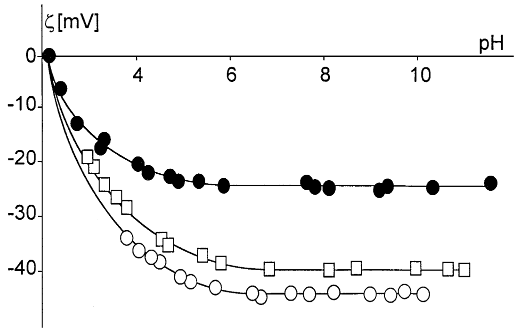


Fig. 7 pH-dependence of the zeta potential of bare silica powders in aqueous KCl solutions of different concentration c^{∞}. ● $c^{\infty} = 10^{-2}\,\mathrm{mol\,l^{-1}}$; □ $c^{\infty} = 10^{-3}\,\mathrm{mol\,l^{-1}}$; ○ $c^{\infty} = 10^{-4}\,\mathrm{mol\,l^{-1}}$

Therefore, the correlation in Fig. 9 supports that the adsorption of OH^- ions takes place on the PCPD patches of the hybrid particle surface. In addition to this effect, silica areas without polymer protection undergo dissociation reactions known from the bare silica surface. The dissociation mechanism is dominant at rather low pH values while the OH^- adsorption is observed as an additional charge generation process at higher pH values.

The second experimental result is, that an increase of the PCPD content of the hybrid particle surface shifts the isoelectric point to higher pH values (Fig. 10).

Obviously, the PCPD chains occupy some of the silanol groups. This can be explained by a steric shielding, as well as by the formation of both coordinative and covalent Si–O–C bonds.

The Freundlich behaviour of the OH^- ion adsorption gives the possibility to separate the two different charge

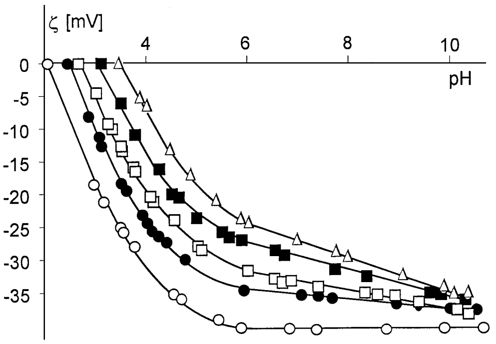


Fig. 8 Dependence of zeta potential on pH values of a 10^{-3} mol l^{-1} KCl solution. CPD was polymerized on the silica surface with triphenylmethyl bromide as an initiator. ○ $y = 0$ w/w% C; ● $y = 2.35$ w/w C; □ $y = 7.3$ w/w% C; ■ $y = 12.5$ w/w% C; CPD was polymerized with trifluoroacetic acid as initiator: △ $y = 17.3$ w/w% C

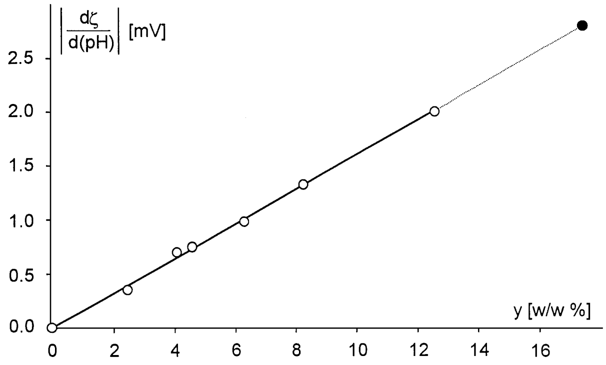


Fig. 9 Dependence of the slope $|d\zeta/d(pH)|$ on the amount of PCPD (as carbon content y) grafted on silica surfaces. ○ initiator: triphenylmethyl bromide/silica, ● initiator: trifluoroacetic acid

generation mechanisms dissociation and OH^- ion adsorption. To discuss the Brønsted acid–base properties of the novel hybrid materials the dissociation reaction as well as specific ion adsorption were quantified separately by means of the double layer model explained above.

Figure 11 shows the dependence of the pK_a values of the residual silica patches on the degree of surface covering by PCPD.

The adsorption potential of the OH^- ions in 10^{-3} mol l^{-1} KCl on bare silica was found to be $\Phi_{OH^-} = -74.8$ kJ mol^{-1}. The corresponding pK_a value was 2.64. The values found are in a good agreement with the values found by Sidorowa et al. [22]. The PCPD patches on the silica surface lower the Brønsted acidity of the remaining silanol groups.

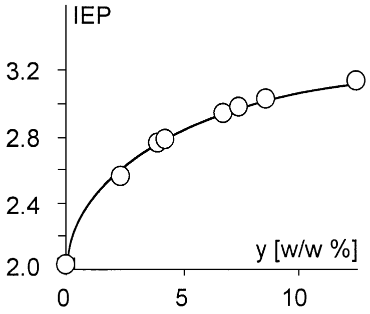


Fig. 10 Shift of the isoelectric point (IEP = pH$|_{\zeta=0}$) as a function of the amount of PCPD grafted on silica surfaces (initiator: triphenylmethyl bromide/silica)

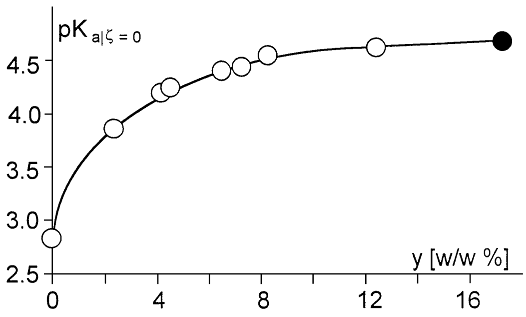


Fig. 11 Dependence of pK_a values of the PCPD–silica hybrid surface on the degree of coating with PCPD. ○ initiator: triphenylmethyl bromide/silica, ● initiator: trifluoroacetic acid

Therefore, it is assumed that the grafting polymerization of CPD monomers starts from the most acidic surface centres. These centers are nuclei where the initiator is very active, and the surface polymerization proceeds from these sites.

The adsorption potentials of the OH^- ions on the polymer-covered silica surface were found between -45 and -20 kJ mol^{-1} depending on the polymer amount on the silica surface.

Solvatochromic investigations

Electrokinetic studies are a useful tool to investigate the Brønsted acid–base properties in aqueous media.

However, water is not present during the polymerization. Therefore, it is appropriate to investigate the Lewis acid–base properties of bare and coated silica particles even in aprotic solvents.

$Fe(phen)_2(CN)_2$ is a well-suited solvatochromic compound. Its long-wave absorption in the visible region strongly depends on the Lewis acidity of the solvent [30–33]. This acidity can be expressed in terms of a Gutmann acceptor number (AN) [33]. The coordination of acidic centres of solvents or solid surface groups at the

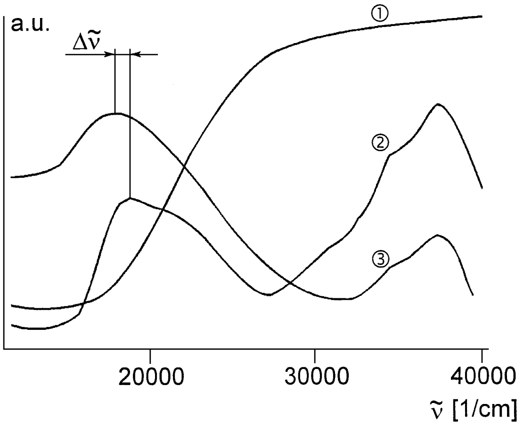


Fig. 12 Difference UV/VIS-reflectance spectra of $Fe(phen)_2(CN)_2$ adsorbed on bare silica ② and on PCPD (17)–silica ③ against silica and PCPD (17)–silica, respectively. ① is the UV/VIS-spectrum of PCPD (17)–silica-composite against bare silica

cyano group of $Fe(phen)_2(CN)_2$ lowers the energy level of the d orbitals at Fe^{II}. Increasing the AN of the medium the metal-to-ligand charge transfer (MLCT) absorption of $Fe(phen)_2(CN)_2$ is shifted hypsochromically [34, 35]. The linear relationship between AN and $\tilde{\nu}_{max,MLCT}$ is given by Eq. (17).

$$AN = 13.698\,\tilde{\nu}_{max,MLCT}[Fe(phen)_2(CN)_2]\,10^{-3}\,cm - 207.8, \quad (17)$$

where $\tilde{\nu}_{max,MLCT}$ is the wave number of the metal-to-ligand charge transfer absorption.

Correlation (17) was re-examined for 27 different solvents by Spange et al. [36], the correlation coefficient was found at $r = 0.987$.

Figure 12 shows the UV-VIS reflectance spectra of $Fe(phen)_2(CN)_2$ adsorbed at bare silica and at PCPD–silica particles with 17.3% carbon content on the surface.

The bathochromic shift of the $Fe(phen)_2(CN)_2$ absorption from silica to PCPD(17.3)–silica indicates a decrease of the Lewis acidity of the accessible surface sites bearing bare silica area. The extent of the shift corresponds to a decrease of the acceptor number from $AN_{silica} = 49$ to $AN_{PCPD(17.3)-silica} = 43$. In the case of PCPD–silica particles with low coverage (w/w% $C < 10\%$) $Fe(phen)_2(CN)_2$ is not sensitive enough to determine changes in the surface acidity of residual silanols in organic solvents.

These results underline that the surface properties of PCPD–silica are more significantly influenced by water than by aprotic liquids.

Conclusions

Coating of silica particles by cationic surface-polymerization with CPD as a monomer yields PCPD–silica hybrid particles with controllable Brønsted acidic centers.

XPS investigations showed that the PCPD chains contain alcohol and carbonyl groups. These reactive groups are introduced by secondary reactions. They bear a synthetic potential to functionalize chemically the hybrid particle surface.

Fitting of the Si 2p spectra of PCPD–silica composites supports the existence of covalent Si–O–C bonds which were expected by means of solid state $^{13}C\{^1H\}$-CP-MAS-NMR spectroscopy [6]. XPS is a suitable supplementary method to quantify the amount of Si–O–C bonds.

The Brønsted acidity was examined quantitatively by electrokinetic measurements. The degree of coating significantly influences the isoelectric point and the pK_a value of the silica patches on the composite surface and the adsorption free energy of OH^- ions on the PCPD patches. Therefore, electrokinetic measurements are a convenient tool to determine both the acid-base properties of PCPD–silica surface in water and also the adsorption behavior of PCPD patches.

Probe molecules like $Fe(phen)_2(CN)_2$ were used to estimate the acceptor properties of PCPD–silica in organic solvents. At high degrees of surface coating $Fe(phen)_2(CN)_2$ indicates a decreased acceptor strength of the composite material compared to the bare silica surface.

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