General and Inorganic Chemistry

Determination of the concentration of hydroxyl groups on Aerosil surfaces

Yu. K. Ezhovskii and P. M. Vainshtein*

St. Petersburg Institute of Technology,
26 Moskovskii prosp., 198013 St. Petersburg, Russian Federation.
Fax: 007 (812) 598 4595. E-mail: offce@spti.spb.su

The concentration of the hydroxyl groups on Aerosil surfaces was estimated by chemical analysis and IR spectroscopy. The temperature ranges for thermal stability of the OH groups and for their reactivity in surface chemical reactions were established.

Key words: Aerosil, surface; hydroxyl groups; dichloromethylsilane.

The properties of the hydroxyl cover of a surface of amorphous SiO_2 depend on the ability of the OH groups to readily undergo various chemical reactions[1]. Up to now, vast experimental information devoted to the structure of the surface of silicas has been accumulated,[1–5] and a number of procedures permitting highly accurate determination of the concentration of surface hydroxyl groups have been developed (see, for example, Refs. 1, 2, 5, and 6). A procedure that we have proposed for spectroscopic investigation of the chemical reactivity of a solid surface[7] made it possible to estimate the reactivity of the OH groups of silica and single-crystal silicon as a function of the conditions of thermal treatment. However, the problem of determining the concentration and reactivity of these groups[2,8] and the temperature limits for their stability still remains unsolved. The use of compounds containing Si—H bonds as modifying agents extends the capabilities of IR spectroscopy in the studies of the surface of oxides.

Experimental

Samples of silicon dioxide (Aerosil A-175) treated at 200—800 °C and also the products of their subsequent interaction with dichloromethylsilane (DCMS) and dichlorophenylsilane vapors were used in the study.

The IR spectra of the initial and modified Aerosil samples were recorded on a UR-20 spectrometer (East Germany) equipped with a vacuum cell for recording the spectra directly during the treatment of samples.[9] Treatment of a dehydrated silica surface with vapors of dichlorosilanes affords functional groups that are bound to the silica surface by one siloxane bond (type I group: =Si—O—Si(ClR)—H, where R = Me or Ph).[7,9,10] The subsequent rehydration of the modified samples by water vapor produces functional groups of type II,=Si—O—Si(OHR)—H, on its surface, and the band corresponding to the Si—H stretching vibrations shifts by 25 cm^{-1}.[7,9] The absorption bands corresponding to the Si—H bond in the chemisorbed silane consist of two components. To determine the absorption maxima and integrated optical densities of these components, the spectra were subjected to computer processing with minimization by the variable metric method.

The content of chlorine was determined by titration of the solution resulting from treatment of a sample under study with distilled water at ~70 °C followed by treatment with a 0.01 *N* solution of $AgNO_3$ (in the presence of methyl orange as the indicator).[11] The proportion of the =Si—H groups in the modified Aerosil was found using the Tserevitinov apparatus from the volume of H_2 evolved after treatment of the sample with 20% KOH at 70 °C.[11] The total concentration of the OH groups in the initial samples (α_{OH}) was determined using the Grignard reagent.[12]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1757—1760, October, 1997.

Results and Discussion

Analysis of the spectra showed that the interaction of dichlorosilane with Aerosil results in the formation of type I and II functional groups on the surface (ν_{max} = 2205 and 2180 cm^{-1}, respectively). It can be assumed that the latter result from a reaction involving the surface silanol groups that form siloxane bonds with the SiO_2 framework and with the OH groups of the sorbed water, which ensure hydrolysis of the Si—Cl bonds. Based on the stoichiometry of the surface reactions, it can be assumed that the concentration of type I functional groups (C_I) is equimolar to the number of isolated Si—OH groups participating in their formation, whereas the synthesis of each group of type II involves one silanol group and one OH group of the sorbed water. Thus, the concentration of Si—OH group participating in the reaction is equal to

$$C_{SiOH} = C_I + C_{II}, \qquad (1)$$

where C_{II} is the concentration of type II functional groups.

The total concentration of the OH groups on the surface of silica that react with DCMS was found as the following sum:

$$C_{OH} = C_I + 2C_{II}. \qquad (2)$$

The C_I value was determined from the concentration of chlorine on the surface of modified Aerosil.

The C_{II} value was calculated in two ways:

1) from the difference between the concentrations of Si—Cl and Si—H groups (the contents of the Si—Cl and Si—H groups were found by a procedure reported previously[11]);

2) from the data of graphical analysis of the spectral absorption bands corresponding to groups I and II:

$$C_{II} = C_I \cdot D_{II} \cdot \varepsilon_I/(D_I \cdot \varepsilon_{II}), \qquad (3)$$

where D_I and D_{II} are integrated optical densities of the absorption bands corresponding to groups I and II, and ε_I and ε_{II} are their extinction coefficients. The D_I/D_{II} values were calculated by computer processing of the spectra. The ratio of the extinction coefficients was found to be 1.2.

To make the results more reliable, the concentrations of the Si—Cl and Si—H bonds were calculated in parallel runs until the deviations between the results were no more than 10%.

It can be seen from the data given in Table 1 that the concentrations C_I and C_{II} in the samples vary as functions of the temperature of their dehydration. The D_I and D_{II} values provide a fairly accurate quantitative characteristic of their relative concentrations as indicated by the fact that the values of C_{II} found from the data of spectroscopic and chemical analyses coincide (see Table 1).

The dependence of C_I, C_{II}, and C_{Si-OH} on the conditions of the pretreatment of samples is shown in Fig. 1. The shape of these curves can be rationalized based on the previously developed[13,14] views on the structure of the hydrate cover of silica, according to which three types of water molecules sorbed on its surface can be distinguished.

The water molecules bound to the OH groups on the SiO_2 surface by hydrogen bonds and desorbed by evacuation at 20—140 °C do not participate in the reactions with chlorosilanes, because Aerosil was dehydrated prior to the reactions at 200 °C and at higher temperatures.

The molecules of water that form coordination complexes, located in the outer coordination spheres of the surface Si atoms and removed at 140—300 °C, can participate in the reactions with dichlorosilanes.[9]

The relatively high concentration of the Si—OH groups reacting with DCMS (see Table 1 and Fig. 1) also implies that the water molecules bound through coordination bonds are involved in the process. As the total concentration of OH groups on the initial surface (α) decreases (see Table 1), the concentration of type I functional groups (C_I) increases (see Table 1 and Fig. 1); this can be explained by the fact that the proton-donating ability of silanols increases during dehydration of silicas. Apparently, this factor counterbalances the removal of the catalyzing water molecules from the reaction area. The observed decrease in C_I and C_{Si-OH} is caused by the fact that during the thermal treatment of Aerosil at 700—800 °C, the overall concentration of

Table 1. Concentrations and spectral characteristics of functional groups on the surface of silica samples dehydrated preliminarily at various temperatures

Sample	T /°C	α_{OH} /μmol m^{-2}	ν_I(SiH)	ν_{II}(SiH)	D_I/D_{II}	C_I	C_{II}*	C_{II}**	C_{Si-OH}	C_{OH}	C_{OH}/α_{OH} (%)
			cm^{-1}			μmol m^{-2}					
1	200	7.8	2205	2180	1.56	0.90	0.70	0.69	1.60	2.30	29
2	300	5.6	2210	2185	2.12	0.95	0.56	0.54	1.51	2.07	37
3	400	3.4	2212	2190	3.04	1.02	0.44	0.41	1.46	1.90	63
4	500	3.0	2215	2192	3.70	1.10	0.36	0.34	1.46	1.82	61
5	600	2.6	2218	2195	4.45	1.15	0.30	0.31	1.45	1.75	67
6	700	2.3	2220	2195	5.15	1.10	0.27	0.27	1.37	1.64	71
7	800	1.5	2220	2198	5.60	1.03	0.20	0.20	1.23	1.43	95

* From the data of chemical analysis. ** From the data of spectral analysis.

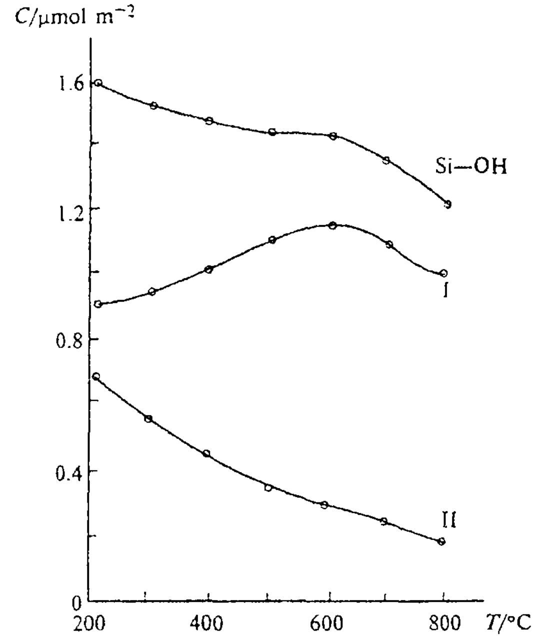

Fig. 1. Variation of the concentration of functional groups of types I and II and Si—OH on silica depending on the temperature of treatment.

silanols on the initial surface decreases.

The water molecules located in the aqua complexes of micropores and characterized by high bond energies are removed in the temperature range of 350—700 °C. Participation of these molecules in the chemical reactions is unlikely due to steric hindrance.

Examination of the results (see Table 1) shows that the concentration of the OH groups that participate in the formation of the functional groups of type I and II is 29 to 95% of the total number of hydroxyl groups present on the silica surface during the reaction. The relatively low contents of reactive hydroxyl groups on the surface of samples that were pretreated at low temperatures can be explained by the fact that the greater part of the OH groups of the water molecules incorporated in the coordination complexes participates in the reaction as a catalyst and is removed with the reaction products. Subsequently the proportion of the reacting OH groups changes only slightly and amounts to 60—70% of their initial concentration.

Despite the fact that the DCMS molecule is capable of forming two siloxane bonds with the surface, no groups bound to the silicon-and-oxygen framework through these bonds were detected during the reaction at 200—250 °C even on the surface hydrated to saturation. Apparently, the stoichiometry of the reactions of chlorosilanes Cl_nSiR_{4-n} (n = 1 to 3) with silica surface depends on the reaction conditions rather than on the density of the hydrate cover.

It was found experimentally that the intensities of the absorption bands due to the type I and II groups decrease and new bands with typical ν(Si—H) frequencies of 2260 and 2270 cm^{-1} appear as a result of prolonged thermal treatment *in vacuo* (~60 min). In addition, in the region of stretching vibrations of the OH bonds, an absorption band corresponding to the isolated Si—OH groups arises at ν 3750 cm^{-1}. The more prolonged thermal treatment results in the disappearance of this absorption band, while the shapes and intensities of the absorption bands corresponding to the Me and Ph groups remain virtually unchanged. Analysis of these qualitative and quantitative changes showed that the appearance of the new bands is caused by the formation of functional groups bound to the surface by two and three siloxane bonds.[9]

Thus, analysis of the IR spectra of hydridesilicas makes it possible not only to evaluate qualitatively the regularities of the variation of the proton-donating ability of the surface silanols but also to determine with high accuracy the concentrations of the OH groups of various types.

The modification of the surface of silicas with chloroalkoxysilanes is used for elaboration of specific adsorbents and fillers for polymers. The choice of the optimal conditions for pretreatment of samples can essentially affect the properties of the final product. Our results demonstrate the character of variation of the structures and concentrations of functional groups depending on the temperature of thermal treatment of samples.

The procedure that we propose for the estimation of the reactivities and concentrations of various types of the OH groups can be used for express analysis in the standardization of silicas used in the production of catalysts, specific adsorbents, and fillers for polymers.

References

1. R. K. Iiler, *The Chemistry of Silicas*, Wiley—Interscience, New York, 1982.
2. A. V. Kiselev and V. I. Lygin, *Infrakrasnye spektry poverkhnostnykh soedinenii* [*Infrared Spectra of Surface Compounds*], Nauka, Moscow, 1972, 459 pp. (in Russian).
3. V. A. Tertykh and L. A. Belyakova, *Khimicheskie reaktsii s uchastiem poverkhnosti kremnezema* [*Chemical Reactions Involving Silica Surface*], Naukova Dumka, Kiev, 1991, 261 pp. (in Russian).
4. Y. H. Hockey, *Chem. Ind.*, 1965, **9**, 5798.
5. L. T. Zhuravlev, *Colloids Surfaces*, 1993, **74**, 71.
6. V. Ya. Davydov, L. T. Zhuravlev, and A. V. Kiselev, *Zh. Fiz. Khim.*, 1964, **38**, 2047 [*J. Phys. Chem. USSR*, 1964, **38** (Engl. Transl.)].
7. Yu. K. Ezhovskii, P. M. Vainshtein, and I. P. Gavrilina, *Materialy VI Mezhdunarodnoi shkoly-simpoziuma po khimicheskoi fizike* [*The VI International Symposium School on Chemical Physics. Reports.*], MATI, Moscow, 1994, 323 (in Russian).

8. V. F. Kiselev, *Poverkhnostnye yavleniya v poluprovodnikakh i dielektrikakh* [*Surface Phenomena in Semiconductors and Dielectrics*], Nauka, Moscow, 1970 (in Russian).
9. P. M. Vainshtein, Yu. K. Ezhovskii, S. I. Kol'tsov, and E. A. Ivanova, *Zh. Fiz. Khim.*, 1983, **57**, 1728; P. M. Vainshtein, S. I. Kol'tsov, and Yu. K. Ezhovskii, *Zh. Fiz. Khim.*, 1983, **57**, 1733 [*Russ. J. Phys. Chem.*, 1983, **57** (Engl. Transl.)].
10. A. A. Chuiko, V. A. Tertykh, V. A. Khranovskii, and Yu. P. Egorov, *Teor. Eksp. Khim.*, 1966, **2**, 247 [*Theor. Exp. Chem.*, 1966, **2** (Engl. Transl.)].
11. K. A. Kreshko and V. N. Borkh, *Prakticheskoe rukovodstvo po khimicheskomu analizu kremniiorganicheskikh soedinenii* [*Practical Guide for Chemical Analysis of Organosilicon Compounds*], Goskhimizdat, Moscow, 1964 (in Russian).
12. N. G. Roslyakova and V. B. Aleskovskii, *Zh. Prikl. Khim.*, 1966, **9**, 795 [*J. Appl. Chem. USSR*, 1966, **9** (Engl. Transl.)].
13. A. A. Chuiko and V. A. Tertykh, in *Adsorbtsiya i adsorbenty* [*Adsorption and Adsorbents*], 1975, 3, 69 (in Russian).
14. Yu. I. Gorlov, V. G. Golovatyi, N. M. Konoplya, and A. A. Chuiko, *Teor. Eksp. Khim.*, 1980, **16**, 202 [*Theor. Exp. Chem.*, 1980, **16** (Engl. Transl.)].

Received November 20, 1996;
in revised form April 29, 1997