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THERMOGRAVIMETRIC STUDY OF SILICA WITH A CHEMICALLY MODIFIED SURFACE

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Thermal methods were used to determine the thermal stability of organic groups introduced into the surface of silica precipitated following its reactions with dimethyl-dichlorosilane (DDS), methyltrichlorosilane (MTS) and methyltriethoxysilane (MTES).

It was found that modification with MTS or DDS leads to a permanent hydrophobic film on the silica surface.

Precipitated silica contains a considerable proportion of reactive surface groups. These groups react quite readily with alcohol and/or various organic silianes. This leads to the possibility of different changes of the chemical and physicochemical properties of the silica preparations, and in particular samples with hydrophobic properties can be obtained.

The thermal stability of organic groups combined with a silica surface is an essential parameter from the point of view of the application of silica free of water (e.g. as rubber mix fillers or components of lubricants). This thermal stability has been examined previously by means of IR spectroscopic methods [1, 2] and thermal analysis [3, 6]. It has been found that the thermal stability of the hydrophobic coating depends on the type of modifier used or on the way the process was conducted.

In the present paper, thermal methods were used to determine the thermal stability of organic groups introduced onto the surface of silica precipitated following its reactions with dimethyldichlorosilane (DDS), methyltrichlorosilane (MTS) or methyltriethoxysilane (MTES).

Experimental

Preparation and characteristics of samples

The modification of silica by means of MTS (series KH) or DDS (series KHD) was achieved during its precipitation from liquid glass solution. The process was

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conducted in three stages, sulfuric acid being used as the basic precipitating reagent [7]. In the first stage, the complete amount of liquid glass and a part of the sulfuric acid were added simultaneously. In the next stages (cf. Table 1), sulfuric acid was replaced by equivalent amounts of chlorosilanes. After precipitation, the samples were filtered, washed three times with distilled water, dried at 120°, and ground in a ball-mill. Two silanes, obtained by means of precipitation from liquid glass solution (KT–3 and KT–4) with sulfuric acid, were modified with MTES. Reagent in appropriate amount was added to an initially crumbled and dried 120° hot sample, and the sample was then ground in a ball-mill for 1 hour. Symbols of samples and the conditions under which they were obtained are given in Table 1. For all samples, the surface area was determined by means of the "one point" S_{op} method on the basis of the low-temperature adsorption of nitrogen and the capacity of a monomolecular layer of benzene a_m^b on the basis of the isotherm of adsorption of its vapor. The TG–DTA curves, for samples dried at 120° were recorded with an OD–102 derivatograph, with α-Al_2O_3 as a standard, samples being heated in open air at a rate of 5 deg/min.

Analyses in vacuum were conducted with a Mettler thermoanalyser. Samples were initially degasified at 10^{-3} Pa at a room temperature in order to remove physically adsorbed water, and they were then heated at 10^{-3}–10^{-4} Pa at a rate of 4 deg/min.

Results and discussion

Decomposition in open air

Thermal curves obtained with the derivatograph for the unmodified sample (KT–3) and a modified sample (KHD–2) are shown in Fig. 1. For all the samples

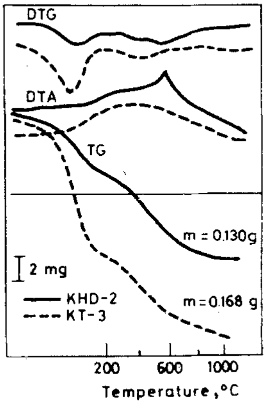

Fig. 1 Thermal curves of silicanes KHD–2 and KT–3 recorded in air.

Table 1 Characteristics of silicane samples and results of thermal analyses in air

Symbol of sample	Method of modification	Amount of silane, mol/kg	S_{op}, m^2/g	a_m^b, mmol/g	Theoretical amount of groups CH_3, % weight**	Mass loss, 200 °, %	Temperature of exothermic effect, °C
KH-1	MTS (III stage)	0.95	157	0.39	1.43	3.7	650
KH-2	MTS (II + III stage)	1.60	144	0.36	2.40	3.7	650
KH-3	MTS (II stage)	0.60	155	0.49	0.90	3.7	650
KHD-1	DDS (III stage)	1.40	135	0.22	4.20	4.3	600
KHD-2	DDS (II + III stage)	2.35	118	0.18	7.05	5.0	600
KHD-3	DDS (II stage)	0.95	142	0.33	2.85	3.6	600
KT-3	—	—	219	0.52	0	3.7	none
KT-3H	MTES	0.22	160	0.33	0.33 (2.97)*	3.8	very weak
KT-4	—	—	206	0.57	0	3.6	none
KT-4H	MTES	0.10	188	0.50	0.15 (1.35)*	3.4	very weak

* in brackets percentage of OC_2H_5 groups is given

** calculated on basis of amount of silane used for modification two stages of mass loss can be observed. The first stage, below 200°, is due to the evaporation of physically adsorbed water. In the second stage, within the range 200–1000° for unmodified silica, water formed as a result of the condensation of siloxy groups evaporates [8], while for modified samples decomposition and deflagration of surface organic groups of type $\equiv Si—CH_3$ (series KH–MTS) and $=Si(CH_3)_2$ (series KHD–DDS) or $\equiv Si—CH_3$ and $\equiv SiOC_2H_5$ (series KT–MTES) also occur. For most samples the TG curves do not show any distinct effects due to the decomposition of organic groups. Only for series KHD, which should contain the greatest quantity of methyl groups, was such an effect observed, at about 600°.

The DTA curves (Fig. 2) show some exothermic effects with endothermic deformation within the temperature ranges where the rate of water evaporaton is highest. Similar DTA curves were reported by Kovol and Firlus [9]. From the heat of desorption of physically adsorbed water (25–42 kg/mol) and the heat of condensation of surface siloxy groups (about 19 kg/mol) [10], one can expect distinct endothermic effects such as those observed with silica gels [11, 12]. The exothermic effects recorded for the tested samples probably result from too great differences between the heating properties of the standard (Al_2O_3) and the highly crumbled amorphous silica (bulk density about 0.1 g/cm^3). For samples modified with MTS, a characteristic exothermic effect can be observed at 650° (cf. Fig. 2a); for samples modified with DDS, the corresponding temperature is 600° (Fig. 2b). This effect was the greater, the higher the quantity of silane used in the reaction, or the higher the quantity of methyl groups in the sample. For samples dehydrated with MTES and containing the smallest quantity of organic groups, this exothermic effect was negligible.

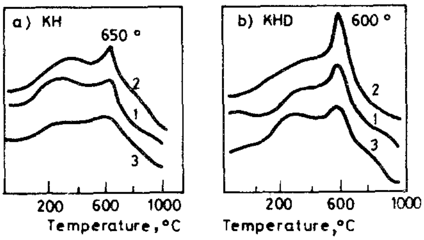

Fig. 2 DTA curves for silicanes of series KHD and KH recorded in air

The observed exothermic effects are due to the decomposition and deflagration of surface $\equiv Si—CH_3$ or $=Si(CH_3)_2$ groups, though such groups are fairly resistant to decomposition. Similar results were obtained by White [2] and Fripiat [6].

Decomposition in vacuum

The results of thermal analyses in vacuum are shown in Table 2 and Fig. 3.

When analyses were performed in vacuum, the initial desorption of physically adsorbed water was practically complete. These observed effects were due to water evaporation (stage I) and to the decomposition if methylsilane groups (stage II). From the TG curves and the pressure changes in the apparatus (curve P) for samples KH-2 and KHD-2, the conclusion can be drawn that the $\equiv$Si—CH$_3$ and $=$Si(CH$_3$)$_2$ groups decompose at temperatures about 130 degrees higher in vacuum than in open air. Comparison of the DTA curves for an unmodified sample and for dehydrated samples shows that, in the former case, the heat effects due to water

Table 2 Results of thermal analyses in vacuum

Sample	Stage I		Stage II		Maximum temperature in pressure curve, °C
	Mass loss, %	Temp. range, °C	Mass loss, %	Temp. range, °C	
KH-2	2.9	100–700	1.0	700–1000	780
KHD-2	3.6	100–600	3.0	600–1000	730
KT-3	3.5	100–1000	none		none
KT-3H	3.5	100–700	0.7	700–1000	750 (500)

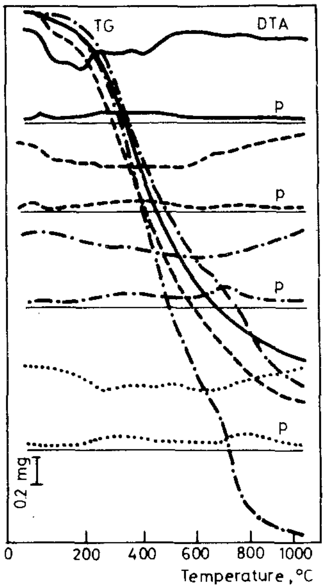

Fig. 3 TG, DTA and pressure curves of silicanes in vacuum. Sample size: 86 mg. ——— KT-3; - - - KT-3H; -.-.- KHD-2; KH-2

evaporation have already disappeared by about 500°, whereas they are still noticeable at higher temperatures for samples treated with silanes. These additional heat effects confirm that the hydrophobic films formed are decomposed.

In the TG and P curves for silica dehydrated with MTES, which can include $\equiv$Si—OC_2H_5 groups, one can observe insignificant effects at about 500°, these effects can signify the decomposition of the above groups in this temperature range.

Conclusions

The study permits the following conclusions:

— The modification of precipitated silica with MTS or DDS leads to a permanent hydrophobic film on its surface.

— $\equiv SiCH_3$ groups are decomposed at 650° in air and $=Si(CH_3)_2$ groups at 600°.

— Destruction of hydrophobic layers in vacuum probably occurs at temperatures higher by about 130 degrees.

— $\equiv$Si—OC_2H_5 groups are decomposed in vacuum at about 500°.

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Zusammenfassung — Thermische Methoden wurden benutzt, um die thermische Stabilität von organischen Gruppen zu bestimmen, die auf die Oberfläche von ausgefällter Kieselsäure durch die Reaktion mit Dimethyldichlorsilan (DDS), Methyltrichlorsilan (MTS) und Methyltriäthoxysilan (MTES) eingebracht wurden. Die Modifizierung mit MTS oder DDS verursacht auf der Oberfläche der Kieselsäure eine permanente hydrophobe Schicht.

Резюме — Термические методы использованы для определения термостойкости органических групп, введенных на поверхность осажденного силикагеля путем обработки его диметилдихлорсиланом, метилтрихлорсиланом и метилтриэтоксисиланом. Установлено, что обработка силикагеля первыми двумя соединениями приводит к образованию на его поверхности устойчивой гидрофобной пленки.