

THERMAL STABILITY OF ORGANOSILICA AND THEIR FORMS MODIFIED BY IONS OF COPPER(II)

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Thermal stability of two-component organosilica sorbents – silico-polymethylsiloxanes with the ratio of hydrophilic and hydrophobic components of 50:50 and 70:30 mass%, and their forms, modified by copper(II), was investigated using thermal analysis (DTG, DTA, TG). The influence of the composition of modified organosilica sorbents and copper(II) content on the endothermic (removal of adsorbed water) and exothermic (decomposition by oxidation of methyl groups, possible hydration of surface) peak temperatures and on mass loss is shown. It was found that thermal stability of organosilica modified by copper(II) was lower than that of initial sorbents and depends on the content of modifying component and ratio of silanol and methylsilil groups in organosilica composition.

Keywords: ions of Cu(II), modified forms, thermal effects, two-component organosilica

Introduction

Knowledge of thermal properties of organosilica sorbents and their modified forms enables to widen their practical application as fillers in paper manufacture, as base for catalysts, indicator powders, and dyes resistant to UV-irradiation. The thermal stability of silico-polyorganosiloxanes was studied by DTA [1]. It was shown that the temperature range of the exotherm, which is attributed to the decomposition of methylsilil groups, was broadened and was shifted into the range of higher temperatures, with decreasing content of these groups in the composition of the sorbents. The endotherm was observed only for samples of organosilica with a high silanol group content in their composition. Earlier we established that with the increase of silanol group content in silico-polyvinylsiloxanes up to 75% by mass, the observed endotherm at 167°C was due to the removal of chemically adsorbed water caused by hydrogen bonds between neighboring silanol groups [2]. In addition, it was shown that total thermal effect (Q_{total}) decreased with the increase of hydrophilic component in the composition of silico-polyvinylsiloxanes. It is well known that the composition of two-component organosilica sorbents and the nature and ratio of hydrophilic and hydrophobic components affect the surface and structural properties of organosilica sorbents and the reactivity of their surface groups [3]. This research is to investigate the effect of modifying organosilica sorbents by copper(II) ions, which are coordinate bonded on the surface [4] and are likely to catalyze the oxidation of surface methyl groups, and also the effect of ion content on the ther-

mal stability of organosilica. The effect of different ratios of silanol and methylsilil groups on the thermal stability of two-component organosilica silico-poly-methylsiloxanes are also investigated.

Experimental

Silico-polymethylsiloxanes (SG-PMS) with different ratio of silanol ($\equiv\text{Si}-\text{OH}$) and methylsilil groups ($\equiv\text{Si}-\text{CH}_3$) 50:50, 70:30 mass%, respectively and their forms modified by copper(II) (3, 30 and 42 mg g⁻¹) were used. These modified forms were obtained by the technique developed by us earlier [5]. DTG, DTA and TG curves of initial and modified organosilica were obtained using Q-Derivatograph (MOM, Hungary). Operating conditions were as follows: the temperature range from 30 to 730°C, heating rate 10°C min⁻¹, sample mass 200 mg, DTA reference $\alpha\text{-Al}_2\text{O}_3$ in air medium using ceramic crucibles.

Thermal effects (Q values) were calculated using the following equation:

$$Q = ASm^{-1} \quad (1)$$

where S – area under thermal peak in the DTA curves; m – mass of sample [g]; A – sensitivity of apparatus. The value of A was calculated from the equation derived on the basis of the apparatus calibration with the help of standard compounds with a well-known thermal effects: $A = 0.0008 T (0.024 T - 1)^{-1}$, where T – maximum temperature of corresponding peak in DTA curves [°C].

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Results and discussion

The results of investigation of thermal decomposition of initial sorbents and their modified forms SG-PMS 50:50 mass% (Cu) and SG-PMS 70:30 mass% (Cu) with different content of copper(II) are given in Fig. 1 (DTG curves) and Fig. 2 (DTA curves). The presence of the endotherm in the temperature range 30–170°C with the maximum at 100–110°C is due to the removal of physically adsorbed water for investigated sorbents of all compositions. It is noted that the endotherm peak area decreased from SG-PMS 50:50 mass% to SG-PMS 70:30 mass% and also on modification by copper(II) (Fig. 2). This is attributed to a decrease in the formation of hydrogen bonds between neighboring silanol groups in SG-PMS 70:30 mass%, due to a decrease in the number of free silanol groups and due to their interaction with copper(II).

The thermal decomposition curves of organosilica sorbents and their modified forms show also that the effect on the exotherm in the temperature range 490–730°C depends on the ratio of hydrophilic (SG) and hydrophobic (PMS) groups and the content of copper(II) (Fig. 1). This peak is due to the oxidation of methyl groups and formation of unstable hydroperoxides as was established earlier [1]. It is found that the exotherm peak temperature decreased from 630 to 610°C with an increase of hydrophilic component (SG) in organosilica composition (Figs 1 and 2). This may be explained by the oxidative

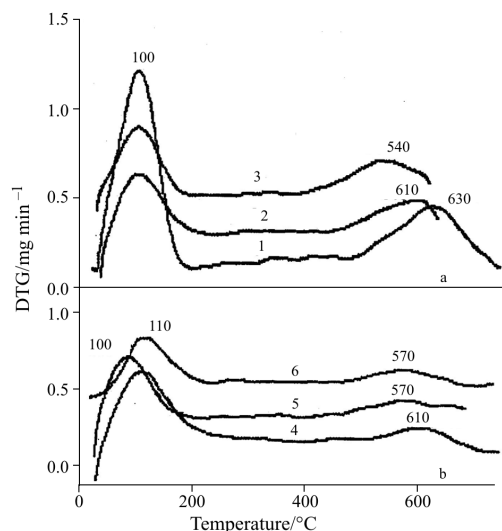


Fig. 1 DTG curves of a – SG-PMS 50:50 mass% and its modified forms and b – SG-PMS 70:30 mass% and its modified forms;

- 1 – SG-PMS 50:50 mass%,
- 2 – SG-PMS 50:50 mass%, (Cu) 3 mg g⁻¹,
- 3 – SG-PMS 50:50 mass%, (Cu) 30 mg g⁻¹,
- 4 – SG-PMS 70:30 mass%,
- 5 – SG-PMS 70:30 mass%, (Cu) 3.0 mg g⁻¹,
- 6 – SG-PMS 70:30 mass%, (Cu) 42 mg g⁻¹

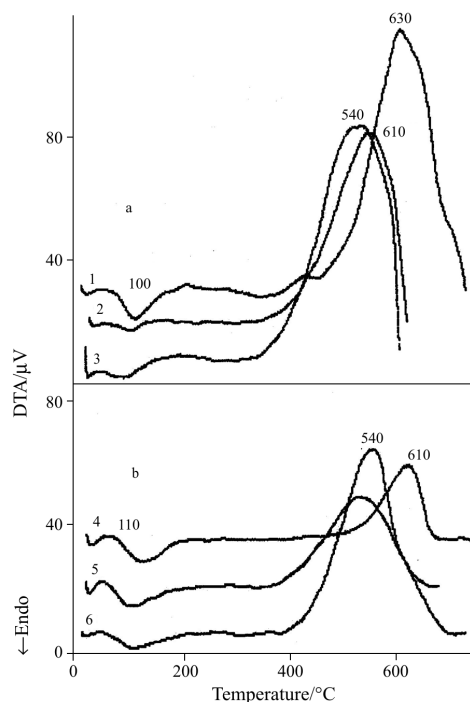


Fig. 2 DTA curves of a – SG-PMS 50:50 mass% and its modified forms and b – SG-PMS 70:30 mass% and its modified forms;

- 1 – SG-PMS 50:50 mass%,
- 2 – SG-PMS 50:50 mass%, (Cu) 3 mg g⁻¹,
- 3 – SG-PMS 50:50 mass%, (Cu) 30 mg g⁻¹,
- 4 – SG-PMS 70:30 mass%,
- 5 – SG-PMS 70:30 mass%, (Cu) 3.0 mg g⁻¹,
- 6 – SG-PMS 70:30 mass%, (Cu) 42 mg g⁻¹

decomposition with $\equiv\text{Si}-\text{C}$ bond breaking, followed both by the removal of methyl groups and hydration of surface with formation of silanol groups. This assumption is supported by the data obtained in the investigation of the oxidation of PMS using IR-spectroscopy [6].

Thermal data and mass losses of investigated organosilica and their modified forms, calculated using DTA and TG curves, are listed in Table 1. The values of Q for removal of adsorbed water decrease from -0.45 to -0.49 kJ g⁻¹ with increasing content of silanol groups in organosilica. In this case, the mass loss in the temperature range 30–170°C decreased from 4.1 to 3.6%. Results obtained are in good agreement with the conclusion that with the removal of hydroxyl groups, hydrophobic homogeneous parts of surface are formed free of silanol groups and with strong siloxane bonds [7].

The mass losses of sorbents in temperature range 170–490°C for SG-PMS 70:30 mass% (2.0%) is greater than for SG-PMS 50:50 mass% (1.0%) and suggest possible dehydroxylation of surface and presence of intraglobule silanol groups of organosilica; the larger the number of such groups, the greater is the content of hydrophilic component of

Table 1 Data treatment of DTA and TG curves of two-component organosilica and their modified forms

Organosilica/mass%	Range of decomposition/°C	Mass loss/%	$T_{\max}/^{\circ}\text{C}$	$Q/\text{kJ g}^{-1}$	$Q_{\text{sum}}/\text{kJ g}^{-1}$
SG-PMS 50:50	30–170 (endo)	4.06	100	–0.45	1.66
	490–730 (exo)	3.05	630	2.11	
SG-PMS 50:50, (Cu) 3.0 mg g ⁻¹	65–135 (endo)	2.0	100	–0.09	1.38
	445–620 (exo)	2.0	610	1.46	
SG-PMS 50:50, (Cu) 30 mg g ⁻¹	40–180 (endo)	2.0	100	–0.76	1.17
	400–610 (exo)	3.0	540	1.93	
SG-PMS 70:30	40–170 (endo)	3.6	110	–0.49	–0.12
	520–700 (exo)	1.5	610	0.37	
SG-PMS 70:30, (Cu) 3.0 mg g ⁻¹	50–140 (endo)	2.0		–0.49	0.34
	460–680 (exo)	2.0	570	0.73	
SG-PMS 70:30, (Cu) 42 mg g ⁻¹	40–140 (endo)	2.0	110	–0.38	0.98
	460–680 (exo)	1.5	570	1.36	

organosilica. The increase of Q values of exotherms from 0.37 kJ g⁻¹ for SG-PMS 70:30 mass% to 2.11 kJ g⁻¹ for SG-PMS 50:50 mass% with increasing of content of hydrophobic component (PMS) of organosilica suggest that oxidative decomposition has occurred. The values of Q_{total} for silico-polymethylsiloxanes decreased with increasing of content of silanol groups in organosilica composition (Table 1) in a similar way for silico-polyvinylsiloxanes [2].

The effect of surface chemistry of SG-PMS and its modification by copper(II) on the thermal stability is as follows: 1) decrease of peak intensity, area under peak in DTA curves, values of Q_{total} , due to the increase of hydroxyl component (SG) for initial organosilica and content of Cu(II) in organosilica composition for SG-PMS 50:50 mass% (Cu) (Fig. 2, Table 1); 2) non-linear dependence of values of Q for SG-PMS 50:50 mass% and approximately linear dependence for SG-PMS 70:30 mass% with increase of copper(II) content (Table 1); 3) the greater shift of the exotherm peak temperature with increasing content of Cu(II) for SG-PMS 50:50 mass% compared with SG-PMS 70:30 mass% (Figs 1 and 2); 4) values of Q_{total} for thermal process decreased for SG-PMS 50:50 mass% and increased for SG-PMS 70:30 mass% with the increase of modifying component, absolute values of Q were less for organosilica with smaller content of methyl groups (Table 1). The reason is that the introduction of ions of copper(II) into the structure of organosilica catalyses the process of polarization of bond $\equiv\text{Si}-\text{C}$ and decreases of maximum temperature of decomposition of modified sorbents with increase of methyl group content. On the other hand, it is attributed to specificity of surface design of these polymer dispersed materials due to local arrangement of alternating silanol and methylsilyl groups (the latter are moving apart) and possible formation of hydrogen bonds between neighboring silanol groups for SG-PMS 70:30 mass%.

Conclusions

Thermal stability of two-component organosilica and their forms modified by copper(II) show the presence of an endotherm (due to removal of adsorbed water) with a peak temperature 100–110°C irrespective of organosilica composition. The exotherm peak area is related to the oxidative decomposition of methyl groups, and possible hydration of surface with formation of silanol groups in the range of maximum temperatures 540–610°C depends on organosilica composition (ratio of silanol and methylsilyl groups) and copper(II) content. The results suggest that the presence of copper(II) in the structure of the two-component organosilica catalyzed the oxidative decomposition of methyl groups and presumably leads to dehydroxylation of surface silanol groups, increasing with the increase of hydrophilic component of organosilica.

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DOI: 10.1007/s10973-006-7588-0