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THERMAL STABILITY OF SILICA-POLYORGANOSILOXANE SYSTEMS

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Abstract

Thermal stability of silica-polyvinylsiloxane systems with different ratio of hydrophilic and hydrophobic components and its forms with adsorbed dyes were studied using thermochemical method. It was shown that the maximum of endoeffect relating to dehydroxylation of sorbents surface is observed at 325°C. The maximum temperature of the second endoeffect depends on the organosilica sorbents composition and increases with a decrease of hydrophilic and hydrophobic sites ratio. It was found that the values of the summary thermal effect lowers upon the raise of the quantity of silanol groups. It was shown that thermal stability of composition materials is higher in comparison with initial organosilica sorbents.

Keywords: dyes, organosilica adsorbent, thermal effects, thermal stability

Introduction

The thermochemical properties of the sorbents play an important role in the creation of new compositions for the adsorption and catalysis, materials with high stability to UV–influence. It is known that thermodestruction polyorganosiloxanes results in the breaking of Si–C bonds whose thermostability depends on the nature of organosilyl groups (phenyl>methyl>ethyl>vinyl) [1]. For polyhydridesiloxane the oxidation of silicon hydride groups occurs above 260°C and is described by exothermal peaks near 384 and 480°C which are assigned to the oxidation of surface and intraglobular silicon hydride groups respectively [2].

In contrast to polyorganosiloxanes two-component silica-polyorganosiloxane compositions have on their surface silanol ≡Si–OH and organosilyl ≡Si–R groups with different ratio of the hydrophilic and hydrophobic components determining surface properties, porous structure, sorption activity, physicochemical characteristics different from polyorganosiloxanes [3]. The thermal stability of silica-polyorganosiloxane systems was not studied.

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This work aims at investigating the thermal stability of silica-polyorganosiloxanes with different composition and the effect of temperature on stability of organosilica sorbents with adsorbed dyes.

Experimental

Silica-polyvinylsiloxanes (SG-PVS) with different contents of the hydrophilic and hydrophobic components (30:70, 50:50, and 75:25 mass%) and silica gel grade KSK–2 (SG KSK-2) were chosen as objects of the investigation.

Such dyes as alcohol-soluble bright-red, induline and acid green antraquinone were used. Compositional materials with dyes based on organosilica sorbents were obtained by adsorption at dye concentrations in the range of $1\cdot10^{-5}$–$1\cdot10^{-4}$ mol l^{-1} and ratio of solid and liquid phase 1:800 at 20°C. For alcohol soluble bright-red and induline alcohol solutions were used. The optical density of dyes solutions before and after adsorption was measured on the spectrophotometer Pye Unicam-8800, pH values of solutions were obtained using pH-meter OP-264/1.

The investigation of thermal decomposition curves of the sorptive materials and their forms, modified by dyes, were studied by thermochemical method using differential scanning calorimeter Setaram (France) in range of temperature 100–600°C. The area of the DSC curves (under the thermal decomposition curves) has been measured by planimeter. The reproducibility of calculations made up ±0.2 cm^2. For the calculation of thermal effects average arithmetical value from some independent calculation was taken. The relative error in the calculation of the DSC curve areas does not exceed 1%. The values of thermal effect was calculated using the following equation: $Q=S\,m^{-1}A^{-1}$, where Q – the value of thermal effect, kJ g^{-1}; S – area under thermal peak, cm^2; m – mass of the sorbent, g; A=142.8 at cell sensitivity 8.4 μV/mW and scale sensitivity 250 μV and 571.4 at scale sensitivity 1000 μV; Q sum. – summary thermal effect, kJ.

Results and discussion

Thermal decomposition curves for sorbents investigated are shown in Fig. 1. Endoeffect at 325°C for SG KSK–2 and SG–PVS with different composition has been observed. It is found that the value of temperature maximum of this endoeffect does not depend upon SG–PVS composition. This thermal effect may be attributed to dehydroxylation of organosilica surface. Maximum temperature of another endoeffect which takes place only for SG–PVS has been dependent on its composition. Thus, changing the hydrophilic and hydrophobic ratios of the sorbents from 30:70 to 50:50 mass% result in temperature shift from 460 to 490°C respectively and more than 500°C for SG–PVS 75:25 mass% (Fig. 1). These data confirmed the fact that Si–C bond is weaker than Si–O bond and suggest the possibility of destruction of vinyl groups on the surface of organosilica sorbent with breaking Si–C bond [1, 4]. Slight endoeffect at 167°C for SG KSK–2 and for system SG–PVS 75:25 mass%, which contains the greatest amount hydroxyl groups among investigated organosilica, is caused by the removal of water adsorbed by the sorbent due to H-bond formation with silanol groups.

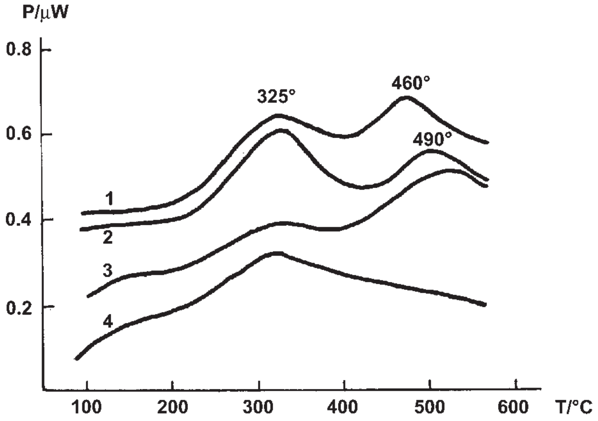

Fig. 1 DSC curves of silica gel KSK–2 (4) and silica gel-PVS systems with ratios of hydrophilic and hydrophobic component: 30:70, 50:50, and 75:25 mass% (1–3 respectively)

Table 1 Thermochemical characteristics of silica and two-component organosilica sorbents

Sorbent	Mass of sorbent/g	Maximum temperature of endoeffect/°C	Area S/cm^2	Value of thermal effect Q/kJ g^{-1}
SG KSK–2	0.0146	325	177.8	1805
SG-PVS 30:70	0.0087	325	58.0	988
		460	40.9	697
SG-PVS 50:50	0.0191	325	17.6	136
		490	51.3	398
SG-PVS 75:25	0.0237	167	8.5	53
		325	29.2	183

The area under thermal decomposition curves was calculated and values of thermal effect were obtained (Table 1, Fig. 2). The results showed that the values of the summary thermal effect decreased with the increase of the content of vinylsilyl groups and with the decrease of the content of silanol groups on the SG–PVS surface. The study of the thermal stability of the two-component organosilica and its samples with adsorbed alcohol soluble bright-red and induline (Figs 3, 4) testifies that the interaction of the surface groups of sorbent with dyes increased on 90°C of the maximum temperature of the first endoeffect of materials based on SG–PVS 30:70 and SG-PVS 50:50 mass% (from 345 to 435°C for alcohol soluble bright-red and from 380 to 470°C for induline respectively).

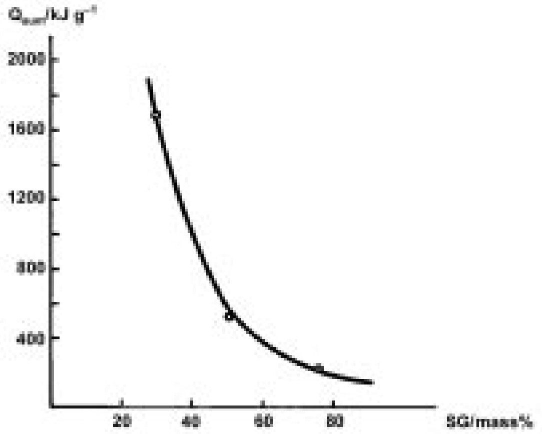

Fig. 2 Influence of SG-PVS composition on the values of thermal effect

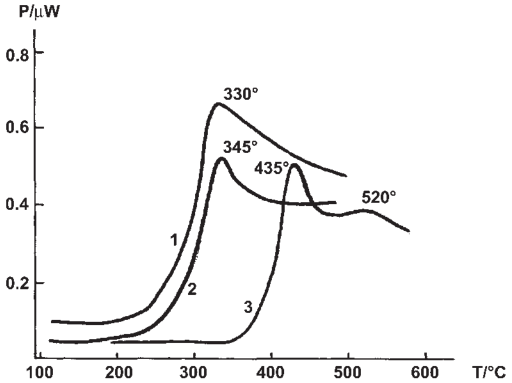

Fig. 3 DSC curves of alcohol soluble bright-red dye (1) and composition materials based on SG-PVS 50:50 (2) and 30:70 mass% (3) with adsorbed dye

The comparative analysis of the DSC curves for organosilica sorbents and their compositional materials with dyes revealed that, from one side, the influence of nature of dyes adsorbed on organosilica causes displacement of maximum of the first endoeffect for sorbent with composition 30:70 mass% SG–PVS in following series:

SG–PVS (325°C)<SG–PVS-alcohol soluble bright-red (435°C)<SG–PVS–induline (470°C) respectively to more thermal stability of composition materials (Figs 1, 3, 4). On the other hand, this displacement of the endoeffect maximum demonstrates the influence of the surface chemistry on the interaction of dyes with active surface hydroxyl and vinyl groups through donor–acceptor specific interaction [3]. The latter indicated the displacement to the region of highest temperature of the second endoeffect maximum observed in the following series for SG-PVS 30:70 mass% (460°C)<SG-PVS 30:70 mass%–alcohol soluble bright-red (520°C)<SG-PVS 30:70

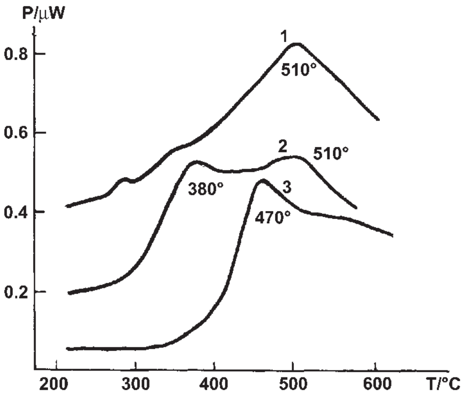

Fig. 4 DSC curves of induline (1) and composition materials based on SG-PVS 50:50 (2) and 30:70 mass% (3) with adsorbed dye

mass%–induline (565°C). Similar changes were established for SG-PVS with the ratio of hydrophilic and hydrophobic components 50:50 mass% but to a lesser degree.

In case of materials with adsorbed acid green antraquinone, changes in composition of SG-PVS did not cause the increase of the thermal stability, which is probably due to the different mechanism of fixing this dye on the sorbent surface and non-linear character of the dependence of the dye adsorption on the composition of organosilica sorbents [5]. Our data showed the absence of influence of pH adsorption on the maximum temperature of thermal effect of compositions with dyes except materials with acid green antraquinone.

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