

EFFECT OF CHEMICAL MODIFICATION OF SILICA SURFACE WITH METAL OXIDES ON THE THERMAL PROPERTIES OF ADSORBED POLYDIMETHYLSILOXANE

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Abstract

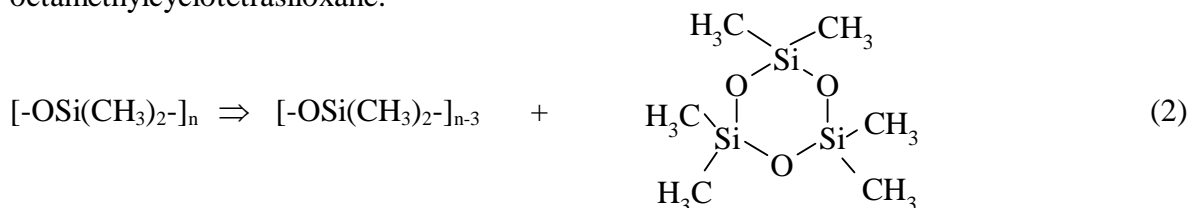
Temperature programmed desorption mass spectrometry, thermogravimetry and differential thermal analysis were used to investigate the thermal destruction of adsorbed polydimethylsiloxane (PDMS) in air and vacuum conditions. Fumed silicas, whose surface contained grafted oxygen compounds of metals or phosphorus, were used as adsorbents. VOCl_3 , CrO_2Cl_2 , TiCl_4 , SnCl_4 , AlCl_3 , PCl_3 and $\text{Zn}(\text{Acac})_2$ vapors were applied as modifiers. It was found that in air the presence of metal oxides and phosphorus on silica surface lead to partial depolymerization of adsorbed PDMS. Degree of depolymerization ranges up to about 80% for V/SiO₂, P/SiO₂ and Al/SiO₂ samples containing 40% PDMS. The presence of metal oxides on silica surface decrease of starting temperatures of Si-C bond destruction in vacuum and result in elimination of methane at 140-550 and 550-850°C.

Introduction

Polymeric composites based on organosilicon compounds and inorganic fillers have a wide application in the production of silicone rubbers, sealants, lubricants etc. [1]. Thermooxidative stability of these materials is one of the major exploitation characteristics. Recently, the modified silica and polydimethylsiloxane (PDMS) have been used for the synthesis of metal oxide-containing hybrid materials [2, 3]. Two main pathways of the thermal decomposition of PDMS exist, depending on the experimental conditions. In air, thermal destruction proceeds via oxidation of methylsilyl groups according to the following reaction scheme [4, 5]:



In an inert atmosphere or in vacuum, depolymerization of siloxane chains is accompanied by formation of the volatile cyclic compounds, mainly hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane:



Thermal decomposition of PDMS on fumed silica surface was a subject of our earlier detailed investigation [6]. It was found that a thermolysis is accompanied by chemisorption of the PDMS decomposition products by silica surface. The preliminary modification of fumed silica by phosphorus oxides essentially affects on the mechanism of PDMS thermal destruction and results in depolymerization of adsorbed macromolecules at the lower temperature [7]. In the present paper, an effect of chemical modification of silica surface by metal oxides on thermal destruction of adsorbed PDMS is considered.

Experimental

Following reagents were applied in our experiments: liquid polydimethylsiloxane PMS-1000, kinematic viscosity 1036 mm²/s at 20 °C (Kremniypolimer, Zaporizhzhya, Ukraine), aerosil A-175, A-300 (Khlorvinil, Kalush, Ukraine). Modified silica was synthesized by interaction of fumed silica with a vapor of chlorides and oxochlorides of various metals (Table) with consequent treatment by water vapor [8-10]. Zinc acetylacetonate was used to obtain silica modified by zinc oxide. PDMS was adsorbed onto silica surface from hexane solution to prepare samples contained 5, 8, 10, 20 and 40 wt. % of the polymer. Thus, the thickness of adsorptive coating of PDMS changed proportionally to amount of polymer in a sample.

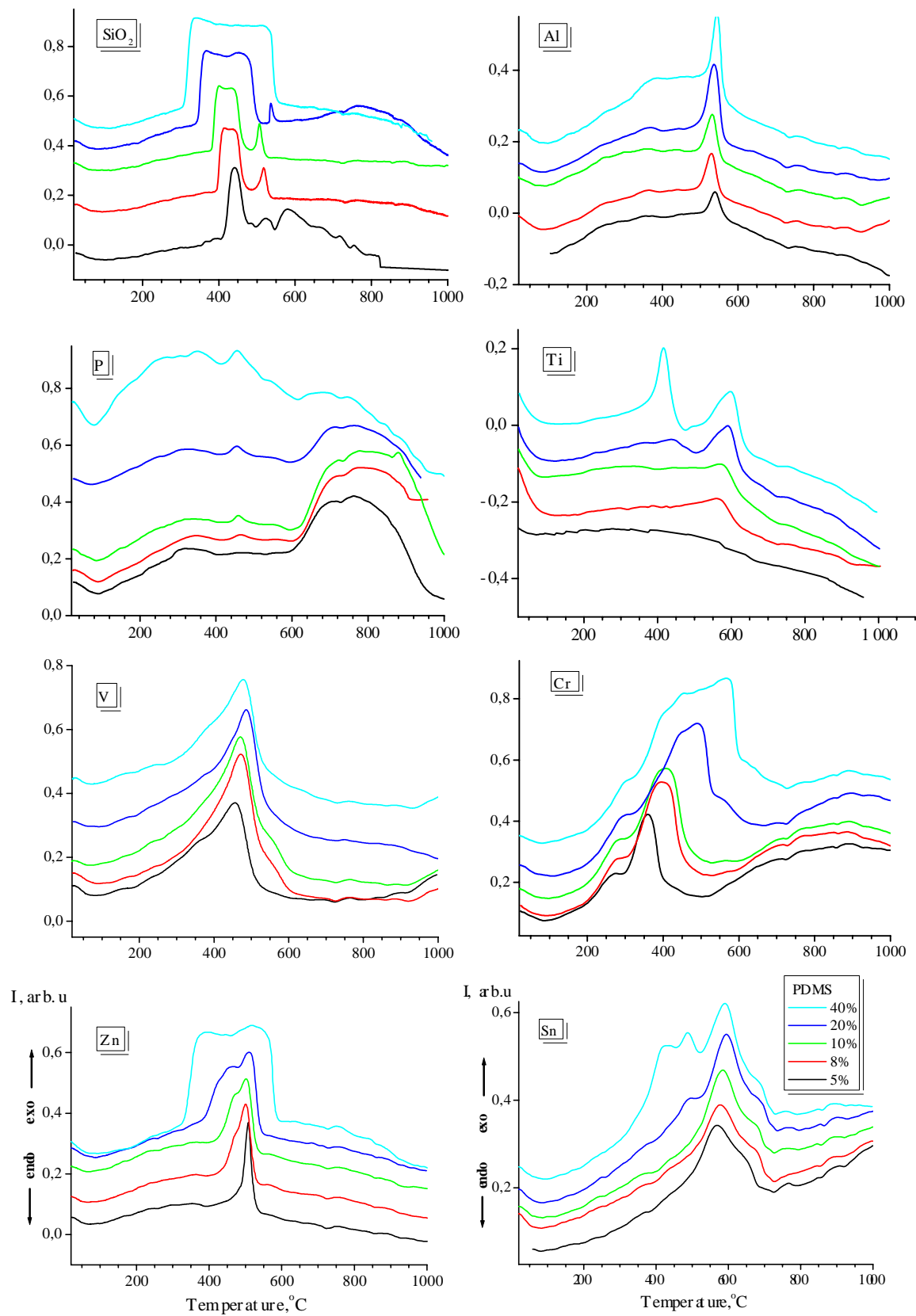
Differential thermal analysis (DTA) and thermogravimetry (TG) were performed using a Q-1500 D (MOM, Hungary) derivatograph. The average sample mass was 272±4 mg. The heating rate was 5 °C min⁻¹. The mass-spectrometric investigations were carried out using mass spectrometer MX 7304A (Ukraine). The sample mass was 2.0±0.3 mg.

Results and discussion

In air, the thermal decomposition of PDMS, adsorbed on the surface of fumed silica, modified by metal oxide, is accompanied by exothermal effects (Fig. 1). An exo-effect at T_{max} 450-650°C corresponds to oxidation of chemisorbed dimethylsilyl groups, which were produced during the thermooxidizing destruction of PDMS [6,7]. It should be noted that intensity and shape of exothermic effects on DTA curves depend strongly on a composition of metal-oxide coating and thickness of PDMS adsorptive layer. When PDMS concentration increases from 5 up to 40%, the broadening of the exo-effect peaks was observed for SiO₂, Cr/SiO₂, Zn/SiO₂ and Sn/SiO₂ samples. Essential broadening of corresponding peaks was observed for Al/SiO₂ and Ti/SiO₂ samples only for surface concentration of 20 to 40% PDMS. The shape and intensity of the exothermic effect is approximately identical for different amounts of polymer adsorbed by the V/SiO₂ sample. The exo-effect, which we assign to decomposition dimethylsilyl groups, is weak in the case of the P/SiO₂ sample. The intense exothermic effect for the phosphorus-containing sample at temperatures higher than 600°C may correspond to formation of surface silica-phosphate structures.

Table. Preparation conditions and characteristics of modified silica samples.

Sample	Modifier	Reaction temperature, °C	Element content, wt. %	BET surface area, m ² /g
V/SiO ₂	VOCl ₃	300	V-2.7	163
Cr/SiO ₂	CrO ₂ Cl ₂	200	Cr(VI)-2.0	161
Ti/SiO ₂	TiCl ₄	200	Ti-1.6	174
Zn/SiO ₂	Zn(Acac) ₂	200	Zn-1.9	181
Sn/SiO ₂	SnCl ₄	300	Sn – 3.5	182



Al/SiO ₂	AlCl ₃	200	Al - 0.8	159
P/SiO ₂	PCl ₃	180	P(III)-1.9	160

Fig. 1. DTA curves of M_xO_y/SiO_2 samples with different amounts of adsorbed PMDS.

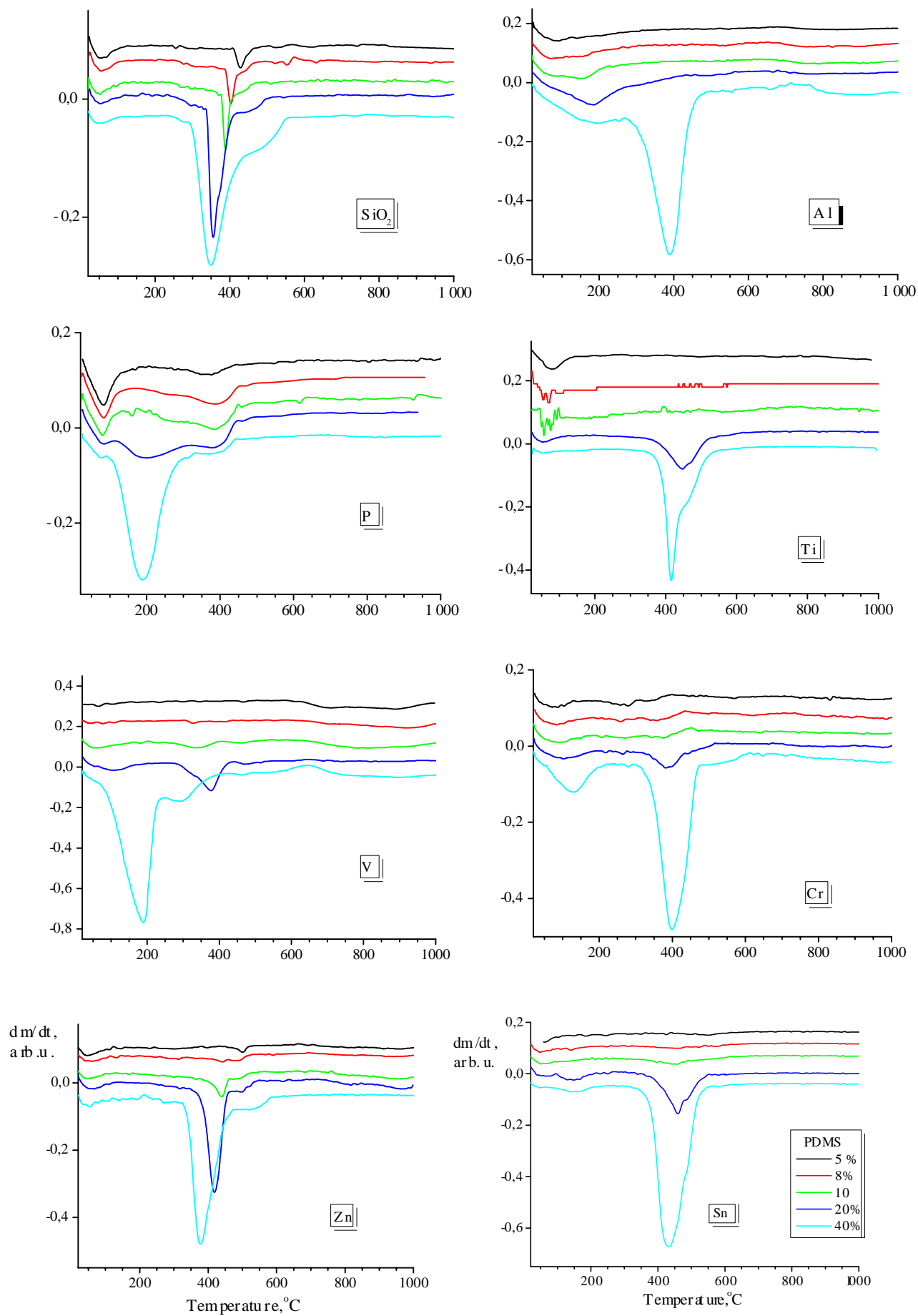


Fig. 2. DTG curves of M_xO_y/SiO_2 samples with different amounts of adsorbed PMDS.

With increasing of thickness of adsorptive layer, the change of displacement of T_{\max} position for the exo-effect did not exceed 50°C for the most of samples. The exception was the sample $\text{Cr}^{\text{VI}}/\text{SiO}_2$, in which the hexavalent chromium was reduced into trivalent in the process of thermal destruction. Thus, T_{\max} of exo-effect was shifted from 350 up to 600°C .

The influence of different metal oxides on thermal oxidizing destruction of PDMS should be compared for the same thickness of adsorption layers. It was found that the maxima of DTA peaks for samples containing 8% of PDMS varied depending on the composition of metal-oxide coating of fumed silica, in the following row:

$\text{P}^{\text{III}}(455^{\circ}\text{C}) < \text{Cr}^{\text{VI}}(480) = \text{V}(480) < \text{pure SiO}_2(500) < \text{Zn}(520) < \text{Al}(545) < \text{Sn}(590) < \text{Ti}(600)$.

TG and DTG curves (Fig. 2) exhibited well-defined region of mass loss at $100\text{--}550^{\circ}\text{C}$, which was attributed to the oxidation of methyl groups and removal of volatile cyclic siloxanes according to reactions (1) and (2). In the samples contained 40% of adsorbed PDMS the greatest mass loss occurred within the interval of $100\text{--}300^{\circ}\text{C}$ for V/SiO_2 , P/SiO_2 and of $370\text{--}550^{\circ}\text{C}$ for SiO_2 , Al/SiO_2 , Ti/SiO_2 , Cr/SiO_2 , Zn/SiO_2 , Sn/SiO_2 . It was found that maxima of these peaks shifted in the sequential series:

$\text{V}(190^{\circ}\text{C}) = \text{P}^{\text{III}}(190) < \text{pure SiO}_2(350) < \text{Zn}(380) < \text{Al}(390) < \text{Cr}^{\text{VI}}(400) < \text{Ti}(415) < \text{Sn}(435)$.

The mass loss in samples under investigation was calculated in accordance with reaction schemes (1) and (2). As for oxidation of dimethylsilyl groups, the calculated value of mass loss was equal 7.6, 3.8 and 1.9% for samples contained 40, 20 and 10% adsorbed PDMS, respectively. In the case of schema (2) PDMS was removed from the sample completely and mass loss was equal to contents of polymer in the sample.

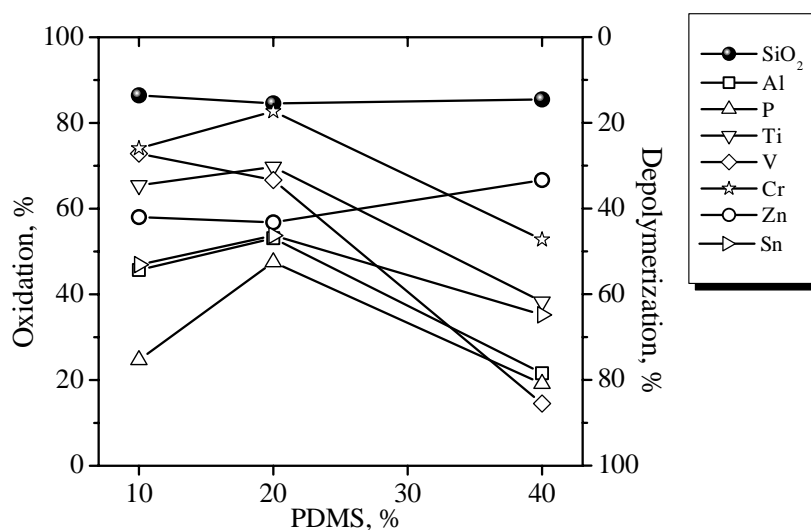


Fig. 3. Conversion degree of PDMS into SiO_2 and volatile cyclic methylsiloxanes according to TG data.

The experimental values of the mass loss for samples of $\text{M}_x\text{O}_y/\text{SiO}_2/\text{PDMS}$ in the interval $100\text{--}1000^{\circ}\text{C}$ were determined. The calculated and experimental data were used to obtain the conversion degree of PDMS into SiO_2 or cyclic organosiloxane (Fig. 3). The experimental data showed that for samples of SiO_2/PDMS the practically complete oxidation of dimethylsilyl groups occurred, according to the reaction (1). Presence of metal oxides on silica surface lead to partial depolymerization of adsorbed PDMS according to the reaction (2).

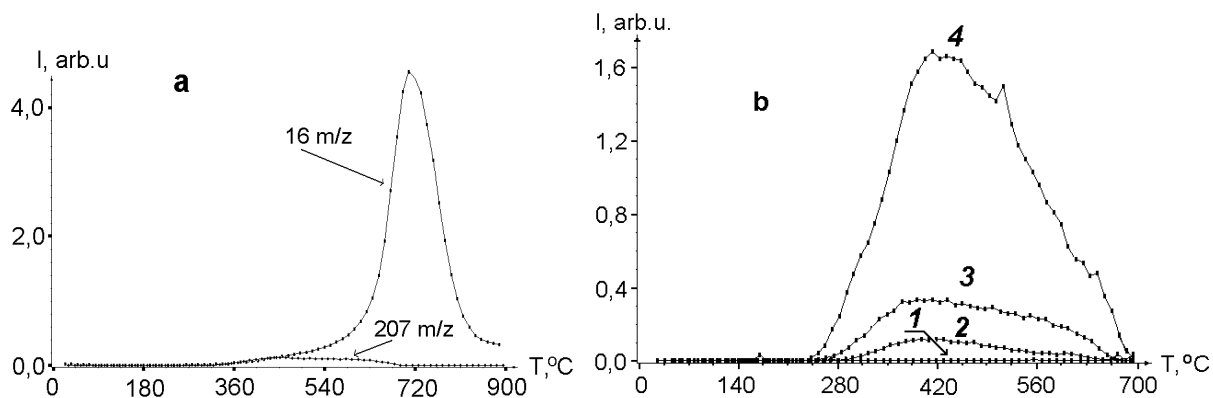


Fig. 4. Mass-spectrometric thermograms for PDMS adsorbed by pure fumed silica: *a* - methane ($16^+m/z$) and hexamethylcyclotrisiloxane ($207^+m/z$) evolution from the sample with 10% of adsorbed PDMS; *b* - hexamethylcyclotrisiloxane ($207^+m/z$) evolution from the samples with different contents of adsorbed PDMS: 1 - 5.3; 2 - 8.8; 3 - 10.2; 4 - 21.2 wt. %

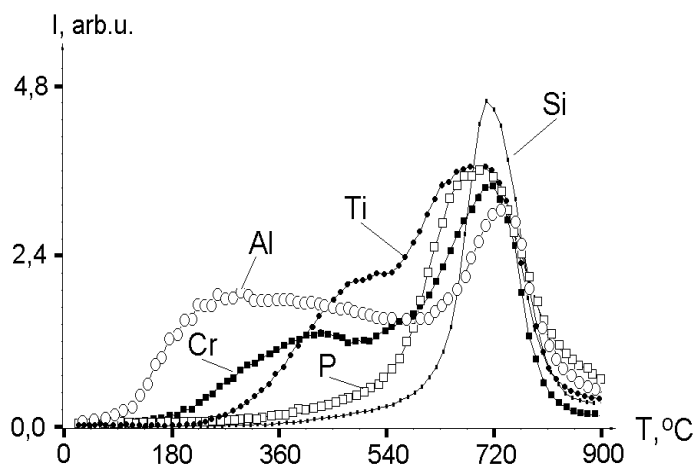


Fig. 5. Mass-spectrometric thermograms of methane ($16^+m/z$) resulting from the destruction of $Me_xO_y/SiO_2/PDMS$ (10%) samples.

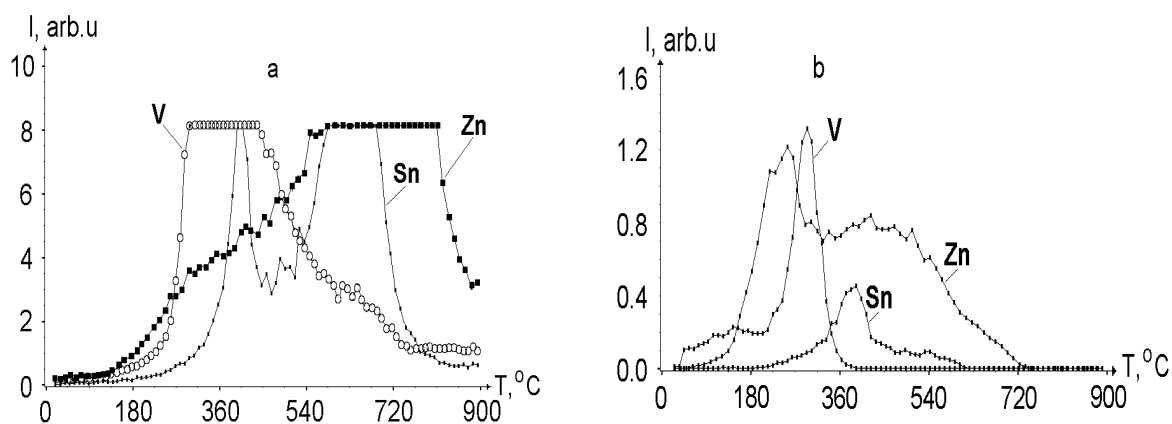


Fig. 6. Mass-spectrometric thermograms for $Me_xO_y/SiO_2/PDMS$ (10%) samples: *a* - methane ($16^+m/z$), *b* - hexamethylcyclotrisiloxane ($207^+m/z$).

Oxides of vanadium, aluminum and phosphorus on silica surface promoted depolymerization of PDMS to greater extent in comparison with other metal oxides. Degree of depolymerization ranges up to about 80% for V/SiO₂, P/SiO₂ and Al/SiO₂ samples contained 40% PDMS.

Thermal decomposition of PDMS in vacuum was analyzed by temperature-programmed desorption mass spectrometry (TPD MS). The thermal destruction of SiO₂/PDMS samples resulted in formation of methane and volatile cyclic methylsiloxanes (Fig. 4). Methane appeared simultaneously with the formation of cyclic products. Mainly, the formation of hexamethylcyclotrisiloxane took place (207⁺ m/z). Contribution of octamethylcyclotetrasiloxane (281⁺ m/z) was less than 10 mol. % in relation to hexamethylcyclotrisiloxane. Formation of cyclic products in TPD MS experiment with polymer adsorbed onto pure fumed silica took place in temperature range 250-700°C (Fig. 4, *b*). However, in the mass-spectrum of the sample, contained 5.3% PDMS, the appropriate to cyclic products signal was not observed. This fact may be explained by adsorption of PDMS molecules in unfolded state. In this case the multidotted adsorption took place, which essentially reduced molecular mobility of polymeric chain and prevented occurrence of loops and rings, necessary for formation of volatile cyclic products.

Modification of silica surface by metal oxides expanded temperature interval of Si-C bond destruction, accompanied by evolving of methane. Figs. 5 and 6, *a* demonstrate that formation of methane in the vicinity of T_{max} at 700-730°C was observed for all samples with the modified surface, except silica modified by vanadium oxide.

Decomposition of Si-C bonds and formation of methane in the region of temperature 200-550°C was specific for each metal oxide. Chemical modification of silica surface with products of polymer chain decomposition occurred during the thermal treatment of the samples. Resulting chemisorbed dimethylsiloxane groups were responsible for the methane formation at temperature higher than 550°C. Appearance of hexamethylcyclotrisiloxane at vacuum decomposition of modified silica samples (Fig. 6, *b*) was observed in wider interval of temperatures than it was observed for unmodified silica. This process began at 140-300°C and was completed at 600-700°C, depending on modified silica composition (for samples with 10 % PDMS).

Conclusion

The thermooxidizing stability of dimethylsilyl groups, chemisorbed on fumed silica surface, depends on composition of modifying metal oxide. The presence of metal oxides in silica surface layer promoted depolymerization of adsorbed polydimethylsiloxane. The presence of metals oxide on fumed silica surface resulted in decrease of starting temperatures of Si-C bond destruction in vacuum and evolution of methane at 140-550 and 550-850°C.

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