Chemisorption and thermally induced transformations of polydimethylsiloxane on the surface of nanoscale silica and ceria/silica

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ABSTRACT

Compositions of polydimethylsiloxane (PDMS) polymer with nanosized silica and ceria/silica were prepared. The influence of these nano-fillers on the thermal stability and degradation mechanism of silicone polymer was investigated using Thermogravimetric Analysis (TGA) and Temperature Programmed Desorption Mass Spectrometry (TPD MS). The results showed that thermal decomposition of pure and adsorbed PDMS differs significantly. The three main stages of the PDMS thermal transformations in the adsorbed state were determined to be: 1) chemisorption of PDMS chains involving the terminal trimethylsilyl groups of the polymer and silanol groups of the silica surface; 2) formation and desorption of cyclic oligomers; 3) high temperature radical degradation of the polymer accompanied by the formation of methane and ethylene. The kinetic parameters of the corresponding reactions were calculated from the TPD MS data. It was found that nanoparticles of cerium dioxide strongly influence the degradation pattern, lower the decomposition temperature and catalyze the formation of methane.

1. Introduction

At present, polydimethylsiloxane (PDMS) is the most frequently used organosilicon polymer and is typically applied in formulations containing fumed silica (SiO_2). Applications of such compositions range from silicone lubricants [1—3] and protective coatings [1—5] to food additives [1,3,6,7], cosmetics [1—3] and pharmaceuticals [1—3,7—14].

The modification of silicon dioxide filler is a common way of improving the properties of silicone polymer composites. For example, addition of nanostructured TiO_2 or ZrO_2 to PDMS/SiO_2-based nanocomposites improves their resistance to thermal degradation; Al_2O_3 improves their conductivity and abrasion resistance [15]. Particles of ZrO_2, V_2O_5, TiO_2, CrO_3, SnO_2 and Al_2O_3 grafted on the surface of fumed SiO_2 strongly influence important characteristics of materials — texture, hydrophobicity and interfacial behavior [16—18]. Therefore, the fundamental properties of compositions PDMS/modified SiO_2 differ considerably from those of PDMS/SiO_2 compositions [16—18].

This paper discusses the kinetics and mechanisms of thermal transformations of PDMS filled with pure silica and CeO_2/SiO_2 nanoscale oxides. Cerium dioxide (CeO_2; ceria) is a rare earth oxide, which due to its many distinctive characteristics, has received much attention in recent years [19—34]. CeO_2 is considered to be the most significant rare earth oxide in industrial applications mainly through its important role in processes of major economic and environmental significance: treatment of gaseous emissions and liquid wastes [19,20], glass-polishing [20], solid oxide fuel cells [21,22], thermochemical production of CO and H_2 [23], steam reforming [24], syngas production from biomass [25], electrochromic thin-film [26—28] and biomedical applications [29—34]. To a large extent, such widespread utilization of the oxide is related to its unique redox properties — it can reversibly release and accumulate oxygen without decomposition. CeO_2 releases oxygen under reduction conditions to form Ce_2O_3 (and a series of reduced non-stoichiometric oxides), which in turn can accumulate oxygen under oxidizing conditions, turning back to CeO_2. As cerium is the most abundant rare earth element and the oxide is simple to produce, large quantities of CeO_2 can be manufactured at relatively low cost. This combined with its low toxicity and biocompatibility has

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led to the rapid commercialization and development of ceria-based materials. As an example, polysiloxane-based composites doped by cerium salts are showing promise in the development of corrosion resistant coatings [35]. Cross-linked polydimethylsiloxane coatings, containing cerium-doped yttrium aluminium garnet particles, have the potential to be used in the next generation of white light-emitting devices [36,37].

The assessment of the role of ceria nanoparticles in the deteriorative reactions that occur during heating of various PDMS/SiO$_2$/CeO$_2$ compositions is the focus of this paper. The thermal decomposition chemistry of simple polysiloxane systems is relatively well studied [38—42], however, still not much is known about thermally induced processes occurring in PDMS composites highly filled with nano-oxides. The identification of mechanisms involved in the degradation reactions is therefore important for any future applications of these materials.

2. Materials and methods

2.1. Materials

Fumed silica A-300 with a specific surface area of 319 m^2/g and primary particle size of ~8 nm in diameter was supplied by a pilot plant of the Chuiko Institute of Surface Chemistry in Kalush, Ukraine. Cerium dioxide precursor — cerium (III) acetylacetonate hydrate was purchased from Sigma-Aldrich. Polydimethylsiloxane — PDMS-1000 (molecular weight $W_m \approx 7960$, degree of polymerization dp = 105; referred to here as PDMS) was purchased from Kremniypolymer, Zaporizhya, Ukraine.

2.2. Preparation of PDMS/CeO$_2$/SiO$_2$ composites

Powders of nanosized CeO$_2$/SiO$_2$ were prepared from anhydrous cerium (III) acetylacetonate (Ce(acac)$_3$) and fumed silica (SiO$_2$) using the method described below. First, Ce(acac)$_3$ was chemisorbed on the surface of highly dispersed SiO$_2$ in a 1 L double-throated round-bottom glass reactor equipped with a mechanical stirrer and refluxing tube. To achieve completeness of the chemisorption reaction, a 1:1 M ratio of Si—OH (surface silanol groups) to Ce(acac)$_3$ was used. For the synthesis, 1.1 g of Ce(acac)$_3$, dissolved in a minimal amount of CCl$_4$, and 5 g of SiO$_2$, previously calcinated at 550 °C, were added to the reactor and stirred at 76 °C under reflux for 1 h. The viscous reaction suspension was then filtered on a Buchner funnel and washed three times with 25 ml of warm CCl$_4$. Before going on to the oxidative calcination stage, the filtrate was dried in air in a Petri dish, and then transferred to a crucible and calcinated in air for 1 h at 550 °C. This caused oxidative destruction of the chemisorbed Ce(acac)$_3$ and resulted in the formation of CeO$_2$ nanoparticles which were homogeneously distributed over the surface of the highly dispersed silica particles. This sample (referred to here as CeO$_2$/SiO$_2$_low) had a 6.6 wt. % of CeO$_2$, a specific surface area (S_{Ar}) of 265 m^2/g (according to low-temperature argon adsorption — desorption measurements) and consisted of amorphous nanoceria (according to X-ray diffraction (XRD) data). The chemisorption and oxidative calcination stages were repeated four times in order to obtain a nano-oxide sample with a higher loading of CeO$_2$ nanoparticles (sample referred to here as CeO$_2$/SiO$_2$_high; 23.3 wt. % of CeO$_2$; S_{Ar} = 189 m^2/g; 3 nm crystalline ceria in a cubic lattice arrangement according to XRD data). The procedure used is also described elsewhere [43].

PDMS was then adsorbed onto samples of pure fumed silica (sample referred to here as SiO$_2$) and the two CeO$_2$/SiO$_2$ nano-oxide samples — with low (CeO$_2$/SiO$_2$_low) and high (CeO$_2$/SiO$_2$_high) ceria content. Before the adsorption, the samples of CeO$_2$/SiO$_2$ and fumed silica were dried at 550 °C for 1 h. Solutions of PDMS in

hexane were then mixed with the oxide samples, stirred for 30 min and dried at room temperature. After evaporation of the solvent, the nominal composition of all PDMS/CeO$_2$/SiO$_2$ samples was: 40/60% wt. polymer/nano-oxide.

2.3. Temperature programmed desorption mass spectrometry (TPD MS)

TPD MS experiments were conducted using an MKh-7304A monopole mass spectrometer (Electron, Sumy, Ukraine) with electron ionization, adjusted for thermodesorption measurements [44]. In a typical measurement a 20 mg sample was placed on the bottom of a molybdenum-quartz ampoule (5.4 mm in diameter and a length of 20 cm), evacuated to ~ 5·10^{-5} Pa at ~ 20 °C and then heated at a constant rate of 10 °C min^{-1} from room temperature to ≈ 800 °C.

2.4. Determination of kinetic parameters from TPD MS data

All kinetic parameters of the chemical reactions on the oxides surfaces were calculated using a specially written computer program which determines the kinetic parameters (the reaction order n, the activation energy E$^{\neq}$, the pre-exponential factor v_0 and activation entropy $dS^{\neq}$) from the TPD MS data [44]. The procedure of obtaining the kinetic parameters from the TPD MS data has been described in a number of studies and reviews [45—48]. Here, we employed a method which uses the linear form of the Arrhenius equation described by Nicholl et al. [45] and in our previous communication [44]. These non-isothermal parameters were calculated from the area of the well-resolved peaks on the temperature scale. The principle behind the program is as follows.

Desorption from a solid surface can be described by the kinetic Equation (1):

$$d\theta/dt = -k_d\theta^n \tag{1}$$

where θ is the surface occupancy (from 0 to 1), t is the time (s), k_d is the desorption rate constant and n is the order of the reaction.

The desorption rate constant can be obtained using the Arrhenius Equation (2).

$$k_d = v_0 \exp(-E^{\neq}/RT) \tag{2}$$

where v_0 is the pre-exponential factor (with units of s^{-1}, for $n = 1$; 1 mol^{-1} s^{-1}, for $n = 2$), E$^{\neq}$ is the activation energy (J/mol), R is the universal gas constant (J/mol·K), and T is the temperature (K).

Substituting Equation (2) into Equation (1), we obtain (3):

$$d\theta/dt = -\theta^n v_0 \exp(-E^{\neq}/RT) \tag{3}$$

If $E^{\neq}$ and v_0 are independent of temperature and surface concentration, the desorption order can be obtained by plotting $ln(\theta^{-n} d\theta/dt)$ against $1/RT$. This plot is used to determine if the reaction order n is equal to either 1 or 2. The correct value gives a linear plot with slope $-E^{\neq}$ ($tg\alpha = -E^{\neq}$) with a high value of the coefficient of determination (R^2 = 0.95—1). Then, we find v_0 by substituting $-E^{\neq}$ into Equation (3) since $ln(v) = E^{\neq}/RT$ at $ln(k_d) = 0$.

The value for the activation entropy $dS^{\neq}$ is found by substituting v_0 into Equation (4):

$$dS^{\neq} = k_b N_A ln(hv_0/k_b T_{max}) \tag{4}$$

where k_b is the Boltzmann constant, N_A is the Avogadro constant, h is the Planck constant, and T_{max} is the temperature of the maximum desorption rate.