

The Dimensional Effect in Trimethylsilylated Silica Nanoparticles

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(Received 14 August 2017; published online 16 October 2017)

The synthesis of organosilicas with a predetermined ratio of trimethylsilyl groups and silanols using trimethyloxysilane and acetic acid as a modifier and catalyst respectively was carried out in this work. It has been established that grafted trimethylsilyl groups influence the structural state of silica. The reducing of the surface tension and, consequently, the Laplace pressure in the SiO₂ globules leads to an increase in the valence angle in the siloxane bridges and the length of Si – O-bond. This dimensional effect in the IR-spectra of modified silica is displayed by displacement of absorption bands in the short-wave region associated with asymmetric (ν_a) and asymmetric-deformation ($\nu_a + \delta_{\text{O-Si-O}}$) vibrations of siloxane bridges.

Keywords: Silica, Siloxane bond, Silanols, Trimethylsilyl groups, Trimethyloxysilane.

DOI: [10.21272/jnep.9\(5\).05030](https://doi.org/10.21272/jnep.9(5).05030)

PACS numbers: 78.30. – j, 78.66.Bf, 81.07.Wx

1. INTRODUCTION

Aerodispersed amorphous silica, obtained in industrial conditions by combustion of silicon-containing substances (SiCl₄, CH₃SiCl₃) in the flame, are widely used as adsorbents in medicine, biology, chromatography, carriers of active substances in the catalysis, polymer fillers, thickeners of dispersion media, etc. [1–5]. Silicas acquired new useful properties as a result of chemical modification of their surface. Simulating the structure of some clusters of silica surface by quantum chemistry methods, it is found that successive substitution of its silanols (hydroxyls) on trimethylsilyl (TMS) (CH₃)₃Si-groups there are substantial change in the distribution of electrostatic potential close to these groupings [6, 7]. Partially trimethylsilylated surface of silica is a bimodal phase, in which there are simultaneously functional groups of two types: hydrophobic (TMS) and hydrophilic (silanols). The hydrophilicity of the silica surface even increases in the initial stages of its trimethylsilylation, due to the formation of the region of negative values of the electrostatic potential localized close to the silicon atom of the grafted group. An increase in the number of TMS-groups is accompanied by a decrease in the size of the region of the negative potential value and the appearance of the maximum of the positive potential, which is localized at the entrance to the hexagonal cavity at sufficiently large distances (3.5 Å) from the silicon atoms, which is also characteristic for the fully trimethylsilylated surface of SiO₂.

Modified silicas containing hydrophilic and hydrophobic groups on their surface can be used as adsorbents for intoxication of the body, wound treatment, removal of heavy metal ions from the aqueous medium, surfactants, etc. They can also be used as stabilizers of emulsified systems or vice versa – as demulsifiers [6].

Currently, polydimethylsiloxane modifiers are used to obtain hydrophobic organosilicas [5, 7]. Polydimethylsiloxane molecules chemisorb on the silica surface at temperatures more 350°C. In these conditions, the

chain molecules, turned into a tangle, are opened and their ends are implanted into any silanols of the surface of SiO₂ particles. Therefore, the chains of these molecules overlap free silanols and prevent to obtain the product with required hydrophilic-hydrophobic balance even with a small amount of chemisorbed modifier.

To prevent this phenomenon, it is to use advisably monomer modifiers for incomplete substitution of silanols. Hexamethyldisilazane (CH₃Si)₂NH is the most attractive for the production of modified silica, whose vapors interact with the SiO₂ surface at 120°C [5]. However, this reagent interacts with both silanol groups of silica and physically adsorbed water molecules [8]. The reaction with water leads to the formation of hexamethyldisiloxane (CH₃)₃Si – O – Si(CH₃)₃, which is practically non-chemisorbed by SiO₂ surface. The concentration of adsorbed water in the surface layer of silica is approximately equal to the concentration of silanol groups. Therefore, the substitution of silanols requires two times the amount of hexamethyldisilazane in relation to the theoretically necessary. Considering its high cost and significant losses when modifying SiO₂, it is necessary to find more suitable reagents for silica silylation. In the present work, trimethylethoxysilane (CH₃)₃SiOC₂H₅ (TMES) was used as a modifier for the preparation of silica with incomplete substitution of silanols. The purpose of this work is to investigate the effect of chemisorbed TMS-groups on the structural state of SiO₂ nanoparticles.

2. PRECURSORS AND METHODS OF ORGANOSILICAS INVESTIGATION

Fumed silica FS-300 (TC U 24.05540209-003.2010), which is produced on an industrial scale by the Experimental Plant of the Institute of Surface Chemistry of the National Academy of Sciences of Ukraine (Kalush), was as the basic silica for chemisorption of TMS-groups on its surface. Its specific surface S_{sp} was 302 m²·g⁻¹ and the concentration of free silanol (hydroxyl) groups – 0.8 mMol·g⁻¹.

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TMES ($(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ (SIGMA-ALDRICH, USA) was used for silica modification. The acetic acid CH_3COOH (chemically pure) was a catalyst for the reaction of the substitution of silanols on TMS-group.

The number of silanols and TMS-groups on the surface of the modified SiO_2 was controlled by IR-spectroscopy using the Specord M-80 spectrophotometer (Carl Zeiss, Germany). The degree of SiO_2 modification θ (in percentages) was determined by the ratio of the optical density of the absorption band of free silanol groups 3750 cm^{-1} in the silica spectrum by the formula:

$$\theta = 100 \left(1 - \frac{D}{D_0} \right),$$

where D_0 and D – the area under the contour of the band with absorption maxima of 3750 cm^{-1} in the basic and modified SiO_2 respectively.

The influence of grafted TMS-groups on the atomic structure of silica nanoparticles was studied by asymmetric and deformation vibrations of siloxane bridges $\text{Si}-\text{O}-\text{Si}$. Infrared spectra of these oscillations were recorded by a Bruker FTIR-ATR spectrophotometer. To achieve the disturbed total reflection in the optical scheme of the device, the samples were applied to the diamond face.

3. RESULTS AND DISCUSSION

Ethoxyalkylsilanes, as well as chloralkylsilanes, react with silanols of the SiO_2 surface at temperatures above 300°C [4, 6]. Among the known modifiers, ethoxyalkylsilanes have the advantage that they are environmentally friendly and do not cause corrosion of process equipment. The trimethylethoxysilane, chosen for modification of SiO_2 surface, boils at 75°C , which allows it to be used in reactions of low temperature gas-phase synthesis.

The search for optimal conditions for the preparation of organosilicas under laboratory conditions was carried out using a 1 L glass reactor equipped with a paddle mixer. The required temperature in the reactor was created by external electric heaters. The speed of the mixer was adjusted in the range from 0 to 1000 rpm.

To reduce the reaction temperature of chloralkylsilanes or ethoxyalkylsilanes with silanol groups, a "third component" is used – a catalyst that reduces the activation energy of the reaction and accelerates the chemisorption process. Organic amines, ethers, ketones, some acids can be the catalyst in these chemisorption processes [6]. The most effective among known catalysts in the reaction of silanols with TMES was acetic acid, which consumption was 15-20 % of the weight of the modifier.

Synthesis of organosilica with a given ratio between TMS-groups and silanols was carried out in the following sequence. The silica in a filled reactor was transferred to a pseudo liquefied state at a mixer speed of 300-500 rpm. The calculated amount of modifier and catalyst was gradually added to the silica at a rate of 1-2 drops per second. Then the temperature in the reactor was increased to $150\text{-}160^\circ\text{C}$. Duration of modifica-

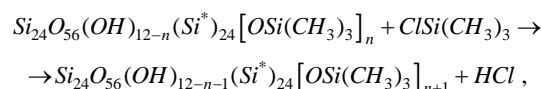
tion was 3 hours. To remove reaction by-products and adsorbed acetic acid molecules from the modified SiO_2 , it was calcined at 300°C for 2 hours. In order to prevent the thermolytic destruction of grafted TMS-groups, argon was fed into the reactor at a rate of $1\text{ L}\cdot\text{min}^{-1}$ during calcination.

Table 1 shows the consumption of TMES for the preparation of organosilicas with different degrees of silanol substitution. The experimental results show that the effectiveness of the modification increases as the degree of silanols substitution increases too. This conclusion is fully consistent with the results of quantumchemical modeling (the method of self-consistent field in the representation of the molecular and a combination of atomic orbitals) of the successive silylation of the hydroxylated surface of the (111) β -cristobalite by trimethylchlorosilane [10]. A cluster $\text{Si}_{24}\text{O}_{56}(\text{OH})_{12}(\text{Si}^*)_{24}$ was as the model, where Si^* – silicon pseudo-atoms, which were added to the periphery of the cluster to compensate the influence of the missing part of the crystalline environment of the volume phase.

Table 1 – TMES consumption for preparation of organosilicas with different degree of silanol substitution

Standard	Consumption of modifier, $\text{mMol}\cdot\text{g}^{-1}$	Degree of silanol substitution, %	Modification efficiency, %
M-30	0.34	27.2	65
M-40	0.42	37.2	72
M-50	0.45	48.3	83

The grafting of TMS-groups into a model cluster can be reproduced by the equation:



where $n = 0 \div 11$.

The enthalpy of this reaction at each stage of successive silylation depends not only on n -value, but also on the position, in which the next TMS-group is introduced in relation to earlier grafted groups.

The simulation of successive silylation of the crystalline cluster surface has shown that at each stage of this process TMS-groups are trying to take positions that are as far apart from each other and at the same distance.

It is important that the negative value of the enthalpy ΔH of the silylation reaction increases from $-82\text{ kJ}\cdot\text{mol}^{-1}$ (for $n = 1$) to $-262\text{ kJ}\cdot\text{mol}^{-1}$ for 7 grafted TMS-groups. The enthalpy value $\Delta H_8 - \Delta H_{12}$, remaining negative, decreases with absolute value for further filled positions ($n = 8 \div 12$). Thus, the results of the simulation of the SiO_2 silylation process indicate that the grafted groups are distributed uniformly on the silica surface and the maximum efficiency of the modification should be expected at 50-60 % of the grafted TMS-groups.

IR-spectra of silica give an opportunity to follow the change in its chemical state during modification (Fig. 1). The intensity of the absorption band of OH-

groups at 3750 cm^{-1} decreases as a result of substitution of the surface silanols on TMS-groups. At the same time, 2968 and 2908 cm^{-1} bands appear in the spectrum, which belong to the asymmetric and symmetric vibrations of atoms respectively, bound by the C–H bond in the methyl groups of the chemisorbed modifier. The redistribution of the intensities of these bands occurs without changing their frequency characteristics as the degree of silylation increases. Interestingly, the band with a maximum at $1635\text{--}1624\text{ cm}^{-1}$, corresponded to deformation vibrations (ν_2) of adsorbed water molecules [11], shifts in the short-wave direction when the number of grafted TMS-groups increases. This indicates on an increase in the polarizing effect of the SiO_2 surface on adsorbed water molecules.

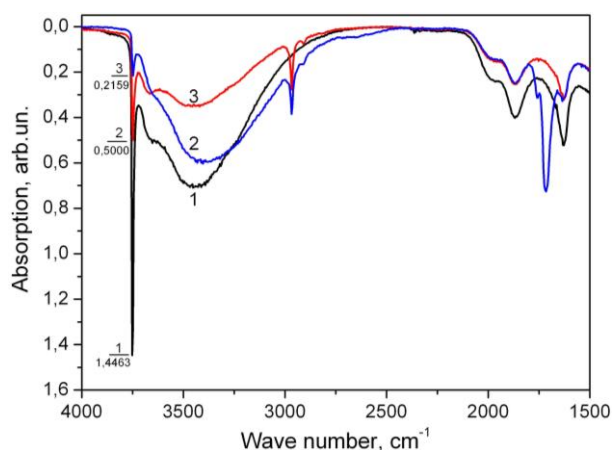


Fig. 1 – IR-spectra of basic silica (1) and organosilica with 48.3 % of TMS-groups after modification at 160°C (2) and calcination at 300°C (3)

The intensive band with a maximum at 1076 cm^{-1} in the basic silica spectrum (Fig. 2), which belongs to the asymmetric vibrations (ν_a) of siloxane bridges Si–O–Si [13], is displaced in the short-wave direction as a result of the grafting of TMS-groups. Its maximum is placed at 1086 cm^{-1} at 48.3 % degree of silanol substitution.

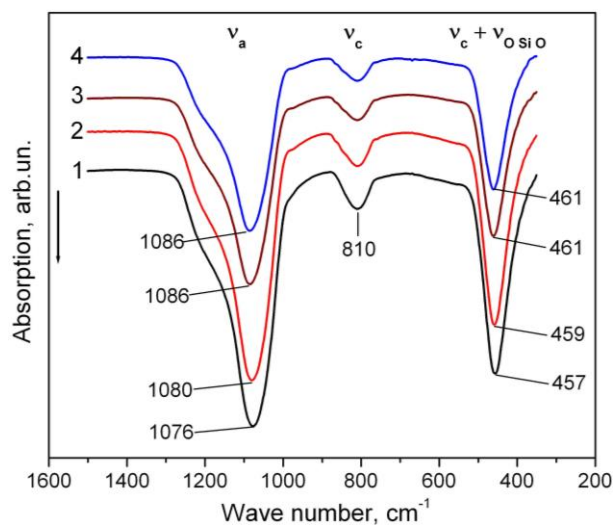


Fig. 2 – IR-spectral bands of asymmetric (ν_a), symmetric (ν_s) and asymmetric-deformation ($\nu_a + \delta_{\text{SiO}}$) vibrations of siloxane bridges in basic (1) and modified M-30 (2), M-40 (3), M-50 (4) silicas

The band at 457 cm^{-1} in the spectrum of the basic sample, which corresponds to asymmetric (ν_a) and deformation (δ_{SiO}) vibrations of siloxane bridges, is also shifted in modified samples in the short-wave direction. The maxima of this band are at 461 cm^{-1} in the spectrum of organosilicas with degree of silanol substitution 37.2 and 48.3 %.

The band with a maximum at 810 cm^{-1} in the spectra of experimental samples, associated with symmetrical vibrations of siloxane bonds, is insignificant in intensity and does not change their position.

It should also be noted, that the area under the contour of ν_a and $\nu_a + \delta_{\text{SiO}}$ spectral bands decreases and their full width at half maximum increases respectively in the first spectral band, while in the second one it decreases, when the degree of silanol substitution increases (Table 2).

Table 2 – Frequency and geometric characteristics of absorption bands of asymmetric and deformation vibrations of siloxane bridges of basic and modified silicas

Standard	ν_a , cm^{-1}	α^* , cm^{-1}	S^{**} , a. u.	$\nu_a + \delta_{\text{SiO}}$, cm^{-1}	α , cm^{-1}	S , a. u.
FS-300	1076	129.2	42.8	457	73.3	20.0
M-30	1080	125.4	40.1	459	71.4	18.2
M-40	1086	135.0	33.6	461	69.4	13.3
M-50	1086	136.9	30.7	461	71.4	13.0

α^* – full width at half maximum;

S^{**} – area under the contour of spectral band.

The results of the IR spectral studies of modified silica in the range of $1500\text{--}300\text{ cm}^{-1}$ indicate the significant effect of grafted TMS-groups on the structural state of the silica matrix.

The authors of this publication have found a phenomenon of dimensional effect in particles of unmodified silica [12]. In fumed silica, when the size of primary particles is reducing, for example, from 56.8 nm ($S_{sp} = 48\text{ m}^2\cdot\text{g}^{-1}$) to 7.1 nm ($S_{sp} = 382\text{ m}^2\cdot\text{g}^{-1}$), in their spectra the ν_a and $\nu_a + \delta_{\text{SiO}}$ bands become wider and shifted to the longwave region from 1119 to 1105 cm^{-1} and from 482 to 467 cm^{-1} respectively. Changes in the structure of fine-dispersed silica are due to the surface tension σ , which leads to an increase in the Laplace pressure in small particles. This pressure is related to the surface tension and the mean diameter of the particles d_p by the equation:

$$p = \frac{4\sigma}{d_p}.$$

In particular, the Laplace pressure increases from 220 to 1160 atm when the average size of SiO_2 globules decreases from 56.8 to 7.1 nm . This pressure, directed from the surface radially to the center of the globules, leads to a decrease in the valence angle in Si–O–Si bridges and the elongation of the siloxane bond. For example, the length of the siloxane bond increases from 1.605 to 1.662 \AA when the angle between the adjacent SiO_4 tetrahedra in Si–O–Si chain from 150 to 120° [14].

The grafting of TMS-groups in modified silica results in a decrease in surface tension and, consequently, a reduction in the value of the Laplace pressure. As a result, the atomic structure of SiO_2 globule relaxes –

the valence angle in the Si – O – Si bridges increases and, accordingly, the distance between the atoms in the siloxane bond becomes smaller.

The relaxed structure of modified silica and the presence of hydrophilic and hydrophobic local areas on the surface give it special physicochemical properties. Experimental verification of the effect of grafted $(\text{CH}_3)_3\text{Si}$ -groups on the physicochemical nature of silica showed that, the organosilica obtained the lyophilic properties due to the substitution of 30-50 % of silanols on TMS groups [15]. In the aqueous medium, the interparticle interaction decreases and the interaction of the particle's surface with the water molecules increases. Modified silica suspensions have higher equilibrium viscosity compared to basic silica ones, moreover organosilica's particles do not lose the ability to thicken the dispersion medium even when their fractal structure is destroyed by the ultrasonic field.

Modified silica with 37.2 % of grafted TMS-groups adsorbs a large amount of water (up to 5 g of H_2O per 1 g of SiO_2) [16]. The surface of this material becomes particularly active (adsorbs nonpolar methane and hydrogen molecules) at a degree of hydration $h = 0.05$ (0.005 g of H_2O per 1 g of SiO_2).

4. CONCLUSIONS

It is set that for obtaining of organosilicas with a predetermined ratio of TMS-groups and silanols, it is expedient to use trimethylethoxysilane as a modifier. The silica modification in a pseudo-liquefied state passes at 150-160°C with the use of acetic acid as a catalyst.

It is found that grafted TMS-groups are uniformly distributed on the surface of SiO_2 globules at increasing of degree of silanol substitution. Maximum efficiency of modification is achieved at ~ 50 % silylation.

The grafted TMS-groups affect the structural state of silica. Reducing the surface tension and the Laplace pressure in SiO_2 globules leads to an increase in the valence angle in the siloxane bridges and the length of the Si – O bond. In the IR-spectra of modified silica, this dimensional effect is revealed by displacement in the short-wave region of absorption bands associated with asymmetric (ν_a) and asymmetric-deformation ($\nu_a + \delta_{\text{SiO}}$) vibrations of siloxane bridges.

Розмірний ефект у наночастинках триметилсилільованого кремнезему

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У роботі проведено синтез органокремнеземів з наперед заданим співвідношенням триметилсилільних груп та силанолів, використовуючи триметилетоксисилан та оцтову кислоту відповідно як модифікатор і каталізатор. Встановлено, що прищеплені триметилсилільні групи впливають на структурний стан кремнезему. Зменшення поверхневого натягу і відповідно Лапласового тиску в глобулах SiO_2 приводить до збільшення валентного кута в силосанових містках та довжини Si – O-зв'язку. В ІЧ-спектрах модифікованих кремнеземів даний розмірний ефект проявляється зміщенням у короткохвильову область смуг поглинання, пов'язаних з асиметричними (ν_a) та асиметричними і деформаційними ($\nu_a + \delta_{\text{SiO}}$) коливаннями силосанових містків.

Ключові слова: Кремнезем, Силосановий зв'язок, Силанолі, Триметилсилільні групи, Триметилетоксисилан.

Размерный эффект в наночастицах триметилсилированного кремнезема

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В работе проведен синтез органокремнеземов с заранее заданным соотношением триметилсилільных групп и силанола, используя триметилетоксисилан и уксусную кислоту соответственно как модификатор и катализатор. Установлено, что привитые триметилсилільные группы влияют на структурное состояние кремнезема. Уменьшение поверхностного натяжения и соответственно Лапласового давления в глобулах SiO_2 приводит к увеличению валентного угла в силосановых мостиках и длины Si – O-связи. В ИК-спектрах модифицированных кремнеземов данный размерный эффект проявляется смещением в коротковолновую область полос поглощения, связанных с асиметричными (ν_a) и асиметричными-деформационными ($\nu_a + \delta_{\text{SiO}}$) колебаниями силосановых мостиков.

Ключевые слова: Кремнезем, Силосановая связь, Силанолы, Триметилсилільные группы, Триметилетоксисилан.

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