Chemistry, Physics and Technology of Surface. 2021. V. 12. N 4. P. 314-325

PACS 68.43.-h; 81.05.Qk; 81.07.Wx doi: 10.15407/hftp12.04.314

P.O. Kuzema, A.V. Korobeinyk, V.A. Tertykh

SPECTROSCOPIC STUDY ON PECULIARITIES OF FUMED SILICA HYDRIDESILYLATION WITH TRIETHOXYSILANE UNDER FLUIDIZED BED CONDITIONS

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail:coralchance@gmail.com

Fumed silica has found widespread application in industry due to variety of fascinating properties. Owing to its specific manufacturing process, it consists of finely dispersed particles and is featured with large specific surface area covered by profoundly reactive silanol groups which are available for chemical grafting. Spherical shape of fumed silica particles and lacking porosity provides a space-filling structure. These characteristics implement the fume silica's utilization as high-surface-area carriers for various catalysts, i.e. metallic nanometer-sized particles, organic moieties, etc. Currently a great attention is called to on-surface grafting to improve the silica-based carrier. Most of research is carried out in area of liquid phase chemistry involving an abundance of expensive and often toxic solvents while the space-filling properties of silica are favoring reactions in fluidized bed conditions.

In current research fumed silica (A-300) was a subject for hydridesilylation with triethoxysilane under fluidized bed conditions. In all synthesis reported in current research the insignificant amount of solvent (1.00 wt. % of the amount used in typical wet-chemical modifications method) was spent for the silica surface silylation. While the mass ratio of silica/TES was kept constant, other conditions, i.e. solvent/catalyst presence, surface pretreatment, additional treatment with water, and the fluidized bed heating mode have been varied. FTIR spectroscopy revealed the interaction between groups of triethoxysilane and silica surface silanol groups and demonstrated the effect of modification conditions on the density of the hydridesilyl groups coverage.

The results of FTIR spectroscopic studies have confirmed the presence of grafted silicon hydride groups on the surface of modified silica, as well as the presence of ethoxy and/or silanol groups – either intact or formed due to hydrolysis of the ethoxy groups. Titrimetric and spectrophotometric analysis was performed to estimate the concentration of grafted SiH groups (in all samples prepared under fluidized bed conditions their concentration ranged within about 0.28–0.55 mmol/g as dependent on the reaction conditions). Other important aspects of fluidization such as the presence of solvent and/or hydrolyzing agent, bed heating mode and the effect of the silica sample thermal pre-treatment are also discussed.

***Keywords**: silica, surface modification, silicon hydride groups, fluidized bed*

INTRODUCTION

Fumed silica (FS) is one of the major chemical compounds of industrial importance and is widely used in many sectors of the economy [1, 2]. Typically, FS is produced as aggregates under high-temperature flame [3]. Conversely to other nanoscopic materials, fumed silica surface is covered with silanol groups, which favor their surface modification. To improve performance, such as specific adsorption properties, redox activity, colloid stabilization, as well as for development of nanostructured materials preparation, *etc*., the FS surface is usually modified with corresponding functional groups [4, 5]. In particular, silica with grafted silicon hydride groups (hydridesilylated fumed silica, HFS) has proved to be active in the processes of reduction in aqueous solutions [6], as well as in the processes of catalytic hydrosilylation of alkene bonds in monomers during their polymerization with the formation of reinforced polymers [7]. Hydridesilylation [8, 9] refers to the reaction of grafting silicon hydride groups on silica surface. The resulting chemically modified fumed silicas containing silicon hydride (≡SiH) groups are called great research attention due to the possibility of reaching relatively high concentration of surface silicon hydride groups (0.4–0.8 mmol/g) [4, 8] and versatile practical application, e.g. metal nanoparticles formation [4], catalytic CO_2 reduction [10], *etc*.

Traditionally, HFSs are synthesized in a liquid-phase manner by chemically modifying the FS surface with triethoxysilane in an organic solvent (e.g., ethanol or acetic acid) [4, 12] followed by filtration (or centrifugation) and drying of the solid phase to remove any solvent residues and reaction products from the surface of the modified silica. This and other methods of HFS fabrication, such as silane thermal decomposition [13], Si(100) etching [14] and even the low-pressure silane plasma clustering [15], are expensive and/or time consuming, therefore the HFS producing with the simplified synthetic protocols is in high demand.

To simplify the procedure and to develop the more cost-effective synthetic methods, we aimed to investigate the process of the HFS fabrication via modifying of FS surface with triethoxysilane without the solvent. Due to the high specific surface area of the FS and a spherical shape of its primary particles the effect of a fluidized bed [11], with a high degree of mass transfer (to attain a relatively uniform distribution of its molecules on the FS surface via modifier addition through dripping or spraying) is achievable with an intensive stirring in the reactor. Subsequent heating of the mixture provides chemisorption of the physically sorbed modifier, removal of low-boiling products of chemical interaction of its molecules with hydroxyl groups of the surface of fumed silica, as well as removal of the residue of the modifier that did not chemically react with surface groups of FS.

The focus of present paper is on the design and operation of the centrepiece of the hydridesilylation process itself, emphasising the reason for choosing fluidized bed rather than typical alternatives such as a liquid phase chemistry in the context of a particular process.

MATERIALS AND METHODS

Fumed silica (A-300) where 300 is the specific surface area (m^2/g) given by the manufacturer (Pilot plant of the Chuiko Institute of Surface Chemistry of NAS of Ukraine (Kalush, Ukraine)), abbreviated in the following text as FS, was used for the studies. FS was used as obtained, and for some samples (noted below, ref. Table) was heated (i.e. pre-treated) at 150 °C for 2 h before the use to remove the adsorbed water [16]. Triethoxysilane (TES, 95 %, Acros organic) and glacial acetic acid (Khimlaborreaktiv) were used without further purification. De-ionized water (DI) was used in all experiments (where required).

Thermal analysis was performed using a MOM Derivatograph (Hungary) with simultaneous record of TG-DTG/DTA curves, in air with the heating rate of 10°/min within the 20–800 °C range. Fourier-transform infrared (FTIR) spectra were recorded for samples mixed with dry KBr (at mass ratio 1:10) using a Thermo Nicolet FTIR spectrometer. UV-vis spectra were obtained using a SF-46 LOMO spectrophotometer (Lenigrad Optical & Mechanical Enterprise). SEM images were captured with a Zeiss Gemini 500 (Carl Zeiss, Germany). The specific surface area of silica was calculated from their low-temperature nitrogen adsorption isotherms using the BET method (Quantachrome AUTOSORB-6B sorptometer, USA).

EXPERIMENTAL

Fluidized bed setup. The main body of the reactor is a three-neck spherical vessel with a mass distributor at its lower end, the distributor being a dished plate. The spherical shape of the vessel is enabling some entrained particles to be returned to be below. Neck of the reactor is equipped with the airlock, and inlets for the modifier injection and thermocouple attached to control the temperature of reactor. Whole reactor is insulated in order to maintain the reaction temperature constant. Since the primary variable in fluidized “solid-emulsion” is a solid-to-modifier ratio [11], the dependant variables, *i.e.* catalyst, solvent, heat mode requires a trial-and-error approach. In the research reported, the silica-to-modifier mass ratio was kept constant and an influence of other conditions (temperature regime, silica surface pretreatment, solvent/hydrolyzing agent presence) on the final product properties were investigated.

Silica surface hydridesilylation (SSH). Chemical modification of FS with TES (Fig. 1.) was performed in the fluidized bed reactor via mass distributor operating at the speed above the minimum fluidization velocity allowing the assembly of solid particles to become fluidized. In all cases the TES/silica ratio was kept as 1 mmol per 1 g and the resulting reaction mixture was heated at 140 °C for 2 h (unless stated otherwise).

Reaction conditions for synthesised samples under investigation are summarized in Table. In the typical procedure 5.0 g of FS (with or without pre-treatment) were placed into the three-neck fluidized bed glass reactor and then at ambient temperature and at fluidization velocity of the mass distributor (1000 rpm) 1.0 mL of triethoxysilane (pure or mixed with a glacial acetic acid (ref. Table)) was added drop-wise (at the approximate speed of 0.5 mL/min) ensuring the homogeneous distribution of the modifier over the bed. Glacial acetic acid was used as non-hydrolyzing solvent for TES to improve its miscibility over the bed and as the FS surface acidifier [4]. The modification was conducted in the fluidized bed reactor for 1 h at ambient temperature. Then the mass distributor was turned to a low velocity mode (300 rpm) or turned off and then reactor was firstly heated up to 90 °C (2 h in order to remove the reaction by-product – ethanol) and then to 140 °C (1 h, to remove the non-reacted modifier and acetic acid, when used). HFS sample obtained via routine wet-chemistry method (in glacial acetic acid) in regards to the method reported elsewhere [6] was used as control (SiH-1).

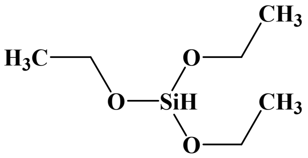

Fig. 1. Triethoxysilane structural scheme

Table. Variation of the SSH procedure

No	Sample denotation	FS mass, g	Surface pre-treatment	TES vol., mL	Acetic acid vol., mL	H_2O vol., mL	Reaction mode
1	SiH-1	5.0	No	0.84	Media, 120	No	Wet-chemistry, 90ºC, 3 h [4]
2	SiH-2	5.0	Yes (150 °C, 2 h)	1.00	No	No	Stirring, 90 °C (2 h), 140 °C (1 h)
3	SiH-3	5.0	No	1.00	No	No	Stirring, 90 °C (2 h), 140 °C (1 h)
4	SiH-4	5.0	Yes (150 °C, 2 h)	1.00	1.00	No	Stirring, 90 °C (2 h), 140 °C (1 h)
5	SiH-5	5.0	No	1.00	1.00	No	Stirring, 90 °C (2 h), 140 °C (1 h)
6	SiH-6*	10.0	No	2.00	1.00	No	No stirring, 90 °C (2 h), 140 °C (1 h)
7	SiH-6rt	5.0	No	1.00	1.00	No	No heating, stirring (3 h)
8	SiH-7	5.0	No	1.00	1.00	0.5	No stirring, 90 °C (2 h), 140 °C (1 h)
9	SiH-8*	20.0	No	4.00	No	1.0	No stirring, 90 °C (2 h), 140 °C (1 h)

* – SiH-6 and SiH-8 samples are made from large samples of FS (10.0 and 20.0 g of FS) therefore volume of triethoxylsilane was increased (2.0 and 4.0 mL, respectively)

Spectrophotometric determination of silicon hydride groups concentration. Spectrophotometric determination of the concentration of grafted silicon hydride groups is based on their reducing activity towards metal ions in solution [4]. Acid aqueous solutions (pH ≤ 3) of molybdates (Mo^{VI}) in the presence of reducing agent are prone to formation of nanostructured "molybdenum blue" (MB) with characteristic blue colour [17]. Despite the fact that MB is in use in analytical chemistry for more than two centuries, the "molybdenum blue" refers not to a single compound but rather to a family of reduced molybdate species with properties strongly dependent on a reducing reaction of their synthesis. Therefore, the UV-vis absorption bands (λ_{max}) given in the literature for MB are ranging from 700 to 750 nm and must be accepted as reference values while the "real" experimental values need to be measured for each analyte. Acidic 2.5 % solution of ammonium orthomolybdate (AO, $(NH_4)_2MoO_4$) was prepared by dissolving of 25 g of AO in the hot DI water (500 mL) followed by filtration and acidification with a glacial acetic acid (50 mL) and volume adjustment to 1000 mL [18] (solution maintains stable for 7 days). The λ_{max} of MB under experimental conditions was determined to be 700 nm (Fig. 2). In order to quantify ≡SiH groups, a calibration curve was built using TES solution as a standard. To each test tube with 4.0 mL of the AO solution the measured amounts of TES (to obtain concentration in a range from 0.1 to 0.8 mmol/L) were added and the total volume was adjusted with isopropanol to 5.0 mL. Test tubes then were placed in a water bath under continuous stirring (300 rpm) for 10 min at 80 °C. Full UV-vis spectra (200–800 nm) were measured in a quartz cuvette (path length 10 mm) against to 4.0 mL of AO solution with 1.0 mL of isopropanol. Fig. 3 shows the calibration curve generated by the method. Said method presented a correlation coefficient for the linear form equal to 0.9961.

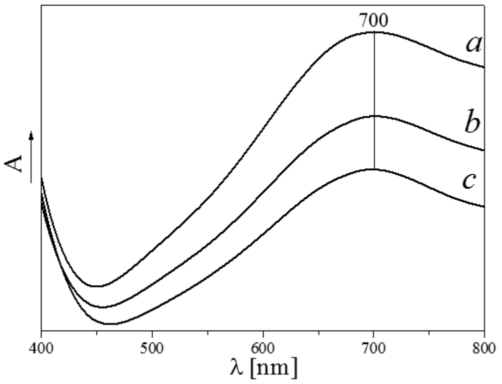

Fig. 2. Typical UV-vis spectra of MB solutions obtained by the reduction of ammonia orthomolybdate solution with silicon hydride groups (*a* – SiH-1, *b* – SiH-8, *c* – TES)

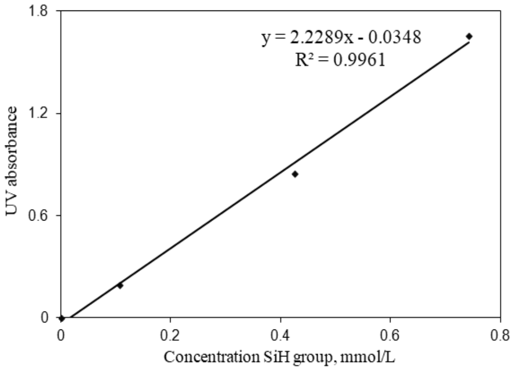

Fig. 3. Dependence of optical density ($l = 1$ cm, $\lambda = 700$ nm) on TES concentration (calibration curve)

The method of spectrophotometric detection of MB formation is based on measuring of absorption at λ_{max} of MB complex with a molar absorption coefficient (ε) for silicon hydride groups slightly higher than 2000 cm^2/mmol (calculated according to the Beer-Lambert Law). For ≡SiH groups quantification in the obtained modified silicas, about 5 mg of the sample in a single run were taken instead of TES used in the technique described above. The concentration of silicon hydride groups (in mmol/g) was calculated using the following formula: $C = A \cdot V/(l \cdot \varepsilon \cdot m)$, where A – the optical density measured; V – the solution volume, cm^3 (5 mL); l – the path length, cm (1 cm); ε – molar absorption coefficient, cm^2/mmol (2229 cm^2/mmol); m – the sample mass, g. For each sample at least three independent runs were carried out.

RESULTS AND DISCUSSION

Scheme of possible FS hydridesilylation with TES via the mechanism of electrophylic substitution of protons in free (isolated) and neighbouring (condensed) surface silanol groups is given in Fig. 4. Three ethoxy groups in a silylating agent (Fig. 1) ensure its high reaction ability towards the silica surface hydroxyls but in turn lead to formation of variable structures as a result of mono-, bi- and three-dentate attachments (Fig. 4 *a*, *b*, *c*). If the reaction media contains enough moisture to hydrolyse the lateral ethoxy groups, then a bridge-like structure (Fig. 4 *a**) formation and elongation of the siloxane chain (Fig. 4 *a***) in the monodentate attachment locations is possible. The grafted ethoxy groups can be partially hydrolyzed with moisture from the air into silanol groups. However, at a sufficiently high concentration of grafted silicon hydride groups (above 0.3 mmol/g), the sample is hydrophobic and is poorly wetted with water. Directed hydrolysis of ethoxy groups via controlled water addition into the modification system will lead to silica hydrophilization due to the substitution of ethoxy groups with hydroxyl groups; however, upon this some part of silicon hydride groups can be hydrolyzed as well.

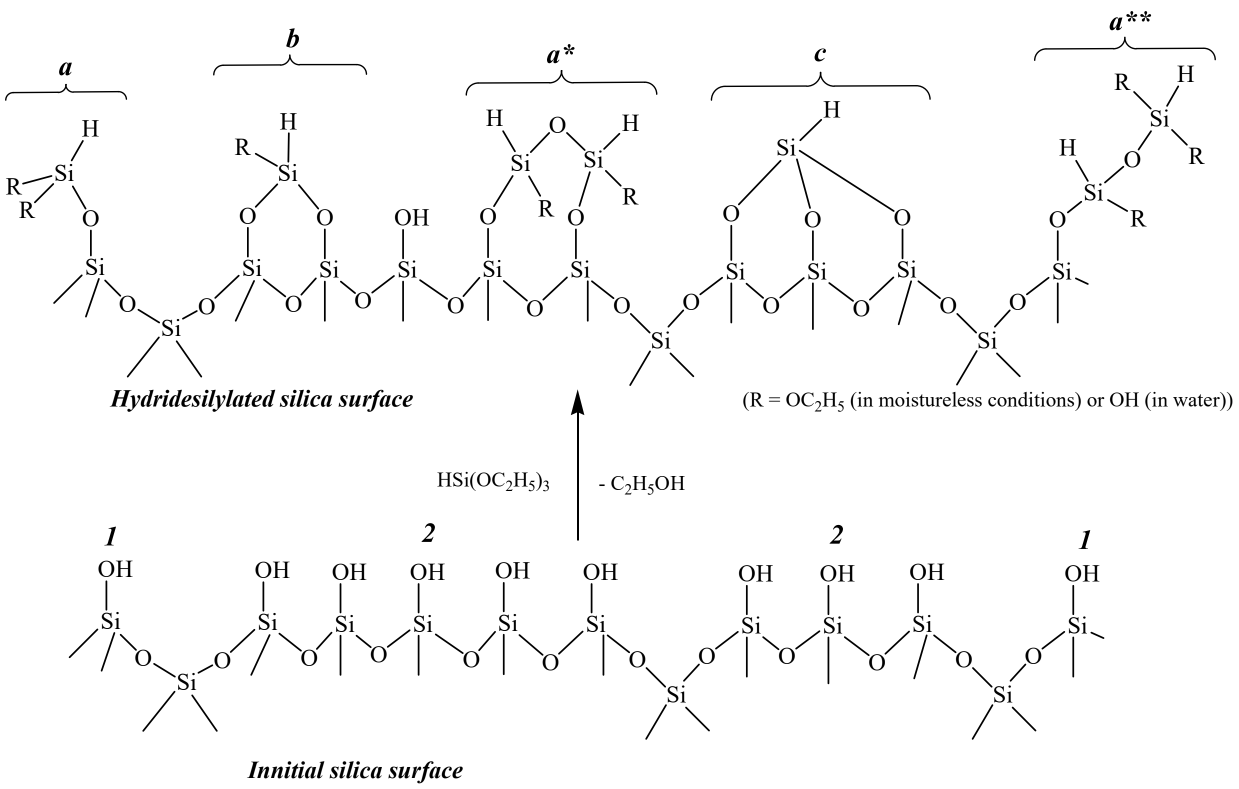

Fig. 4. Scheme of TES interaction with the FS surface through isolated (*1*) and condensed (*2*) silica surface hydroxyls resulting in mono- (*a*), bi- (*b*) and three-dentate (*c*) attachments

Fig. 5 shows the FTIR spectra of A-300 with and without pre-treatment. In the spectra of both silicas the noticeable narrow absorption band is present at 3750 cm^{-1}, characteristic for stretching vibrations of isolated silanol groups [19]. The chemical modification of silica with TES, regardless to the method of silica surface modification (liquid phase or under fluidized bed conditions) causes the decrease in the intensity of the Si-OH mode at 3750 cm^{-1} (Figs. 6–10). The lower intensity of the Si-OH band when compared to unmodified silica, as well as the appearance of absorption bands at 2240–2260 cm^{-1} (stretching vibrations of Si-H groups) and at 2985 cm^{-1} (stretching vibrations of C-H bonds) indicates the presence of surface silicon hydride groups, residual ethoxysilyl groups, as well as free silanol groups – both residual and formed as a result of hydrolysis of ethoxy groups.

When comparing the FTIR spectra of HFS obtained in different ways (liquid-phase or fluidized bed conditions) under other equal conditions (Fig. 6), it is distinctly seen that in both cases the absorption band corresponding to the grafted SiH groups (2260 and 2257 cm^{-1} for SiH-1 and SiH-5, respectively) is quite intense, which may indicate a high degree of grafting of these functional groups to the surface of silica modified via both pathways. The difference in the position of the peak maxima is due to the diverse nature of the substituents at the silicon atom bearing the hydride group, to which the absorption bands νSiH have a high sensitivity [8]. These substituents in the vast majority are hydroxyls in the case of SiH-1 and ethoxy groups – in the case of SiH-5, which is confirmed by the diametrically opposite ratio of intensity νSiOH and νCH (3750 and 2985 cm^{-1} respectively), characteristic of FTIR spectra of these silicas. The solvent (acetic acid) apparently promotes the interaction of ethoxysilyl groups with its molecules according to the scheme: $\equiv SiOC_2H_5 + HO(O)C\text{-}CH_3 \rightarrow \equiv SiOH + C_2H_5O(O)C\text{-}CH_3$. As a result, silanol groups are formed, the revelation of which is observed in the FTIR spectra of SiH-1 sample. In the case of a fluidized bed condition of the HFS synthesis, due to the negligible amount of acetic acid in a system, the influence of the above process is insignificant. Therefore, under the conditions of a fluidized bed using acetic acid as a catalyst for the SSH process, due to the higher concentration of organic groups grafted to the surface, a more hydrophobic sample is obtained than that in the case of liquid-phase method of silica hydridesilylation using acetic acid as solvent and reaction medium.

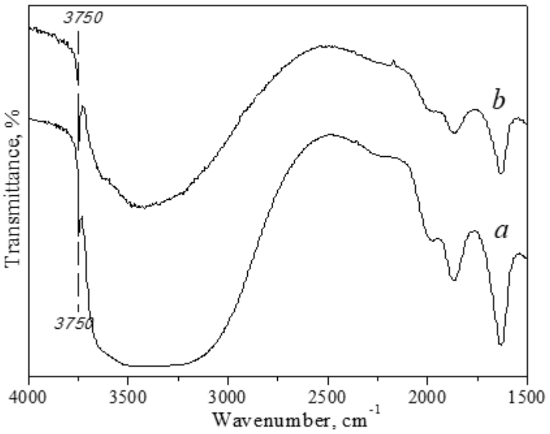

Fig. 5. FTIR spectra of A-300: non-treated (*a*) and pre-treated at 150 °C for 2 h (*b*)

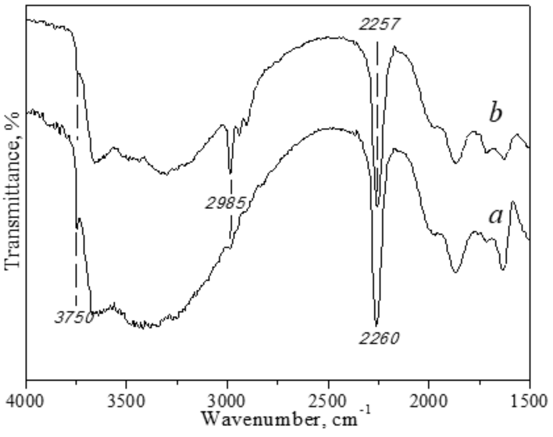

Fig. 6. FTIR spectra of HFS samples obtained via wet-chemistry (SiH-1, *a*) and fluidized bed (SiH-5, *b*) methods

The influence of the FS surface pre-treatment (heat treatment) on the SSH process under the fluidized bed conditions can be determined via the analysis of the FTIR spectra shown in Figs. 7, 8. As can be seen from Fig. 7, in case of modification with triethoxysilane without a catalyst (acetic acid), pre-treatment of the FS surface promotes more complete grafting of organic groups (higher intensity νC-H, Fig. 7 *a*) and substitution of hydroxyl groups (lower intensity νSiOH) probably due to water removal, which is more active agent with respect to ethoxy groups of TES molecules than are the FS surface structural silanol groups.

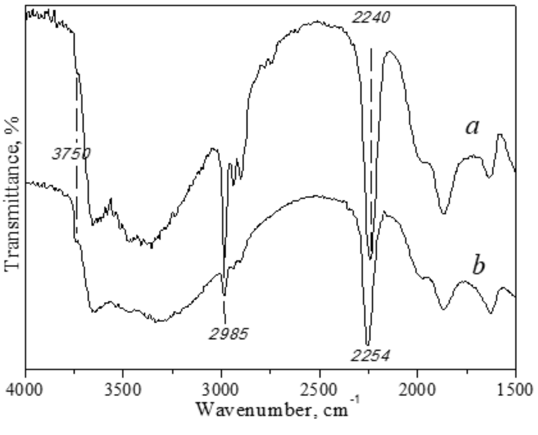

Fig. 7. FTIR spectra of HFS samples obtained via fluidized bed method without catalyst, with (SiH-2, *a*) and without (SiH-3, *b*) the surface pre-treatment

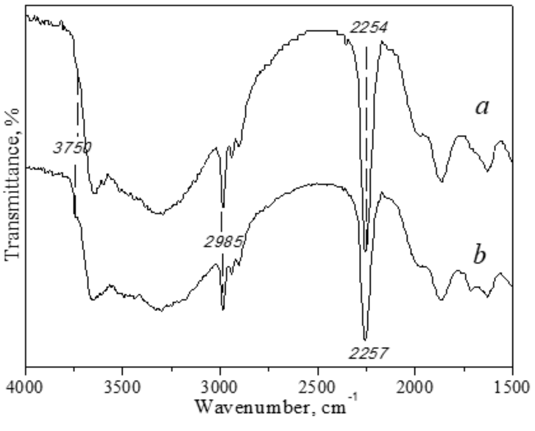

Fig. 8. FTIR spectra of HFS samples obtained via fluidized bed method with catalyst, with (SiH-4, *a*) and without (SiH-5, *b*) the surface pre-treatment

Likewise, the shift of the νSi-H peak maximum to the low-frequency region in the case of SiH-2 (approximating νSi-H in the triethoxysilane molecule [8]) – 2240 cm^{-1}, compared to 2254 cm^{-1} of SiH-3 (Fig. 7 *a, b*), indicates the presence of mainly ethoxy-silicon-hydride groups, disparately, to the case of the sample synthesized from the FS without preheating the surface, where the substituents on the silica atom bearing the hydride group, are hydroxyl groups. The same trend is observed in the case of the acid catalyst utilization. However, this variation is significantly lesser due to the effect of the catalyst on the ethoxy groups conversion into hydroxyls, according to the above reaction scheme. This assumption is confirmed if one compares the FTIR spectra of SiH-2 and SiH-4, as well as of SiH-3 and SiH-5 (Figs. 7, 8). Indeed, in the presence of acetic acid in the modifying agent, the intensity of νC-H decreases, and the maximum of νSiH shifts to the right. It should be noted that the higher intensity of νC-H for the sample SiH-5 compared to SiH-3 and not vice versa, as would be natural if the hypothesis of a decrease in the concentration of ethoxy groups in the presence of acid is correct. This can be explained by the possible contribution of acetic acid to the intensity of νC-H combined with the competitive interaction of acid and adsorbed water on the unheated surface with ethoxy groups.

Stirring of the mixture at the heating stage virtually has no effect on the modification final result under the fluidized bed conditions because the FTIR spectra for samples SiH-5 and SiH-6 (Fig. 9) are roughly identical. This finding is of practically importance because it makes possible (which is crucial) to heat the mixture in the reactor without stirring as it prevents the partial volatilization of the silica from the reaction medium together with vaporous SSH products. As for the effect of heating itself during modification, when comparing the FTIR spectra of SiH-6 and SiH-6rt samples (the latter was obtained at room temperature) (Fig. 9), it can be concluded that at ambient temperature triethoxysilane is only fractionally chemisorbed; on heating, a part of the physically sorbed modifier is removed (the intensity of the νSiH band for SiH-6 is lower than that for SiH-6rt), and an additional substitution of isolated silanol groups with ethoxy-silicon-hydride groups occurs (the intensity of the νSiOH band for SiH-6 is lower than that for SiH-6rt, and the intensity of the νCH band, on the contrary, is higher).

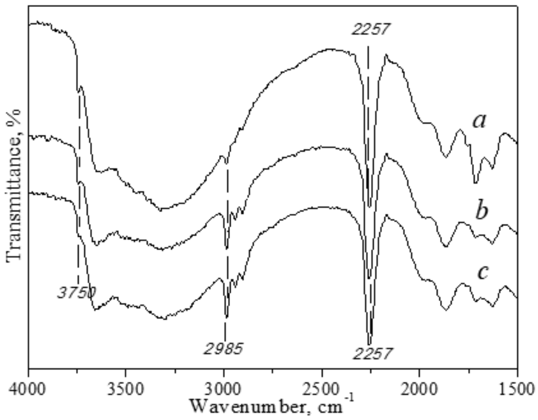

Fig. 9. FTIR spectra of HFSs obtained with catalyst via fluidized bed, without pre-treatment, and: without heating but under 3h stirring (SiH-6rt, *a*), without stirring but under heating (SiH-6, *b*) and with both stirring and heating (SiH-5, *c*)

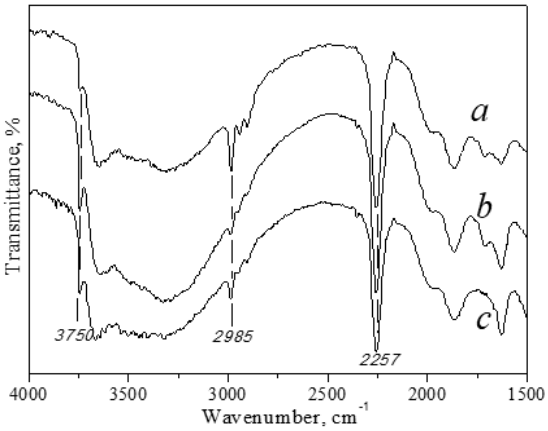

Fig. 10. FTIR spectra of HFSs obtained via fluidized bed, without pre-treatment, and: with heating and no stirring (SiH-6, *a*), with heating and no stirring but with added water (SiH-7, *b*) and with heating and no stirring with added water but without catalyst (SiH-8, *c*)

In order to check the possibility of tuning the resulting sample hydrophobicity level (or hydrophilic-hydrophobic rate), samples were synthesized without (SiH-6) and with (SiH-7) water addition before the heating stage (three times the excess relative to the stoichiometric amount required for complete hydrolysis of ethoxy groups) and the relevant FTIR spectra were analyzed (Fig. 10). As can be seen from the spectra, water partially hydrolyzes the ethoxy groups (νCH intensity decreases in the case of the SiH-7 sample, but the band does not disappear completely) with the formation of silanol groups (νSiOH intensity increases). One should also note only slight decrease in the intensity of νSiH with the addition of water and subsequent heating, so no noticeable hydrolysis of the grafted silicon hydride groups is fixed by

FTIR spectroscopy. The as-obtained hydrophilic-hydrophobic hydridesilylated silica (SiH-7) is immediately wetted upon contact with water, and therefore the approach itself proved to be convenient and effective for solving the task of hydrophilization of customarily hydrophobic HFS. Such hydrophilized silica (SiH-8) can be obtained without the acid catalyst. Fig. 10 shows that FTIR spectra of SiH-7 and SiH-8 are similar; a slightly higher intensity of νCH for SiH-8 compared to SiH-7 may be the result of only two-, not three folds of the water excess taken for hydrolysis of ethoxy groups in the case of SiH-8. However, this sample is relatively easily wetted upon contact with liquid water, as well.

Quantification of grafted surface silicon hydride groups for the samples obtained under current investigation was performed with the iodometric titration (iodometry) and spectrophotometric determination using the molybdenum blue. Spectrophotometric method (Fig. 11) revealed that the sample obtained by the conventional wet-chemistry method (SiH-1) had 0.47±0.01 mmol/g of SiH groups, which is roughly the mean value for samples obtained through experiment without water addition. Employment of the fluidized bed method improves those values for samples SiH-2, SiH-3 and SiH-4 up to 0.5–0.55 mmol/g of silicon hydride groups attached to the surface. However, if one takes into account the reaction yield (the real degree of grafting *vs* the theoretically possible one), it is approximately the same for these four samples (about 0.55). Upon this, the surface pre-treatment (SiH-2 and SiH-4) or the presence of catalyst (SiH-4) does not have statistically significant influence on concentration of ≡SiH groups in the resulting sample. The sample obtained without stirring during the heating in the reactor under fluidized bed conditions (SiH-6) had 0.45±0.03 mmol/g of grafted SiH groups, which is about of mean for this investigation. The water addition during the modification process reduces the concentration of grafted surface silicon hydride groups by up to one and a half times (0.28±0.01 and 0.35±0.01mmol/g of SiH groups for SiH-7 and SiH-8, respectively). This reduction is probably due to the hydrolysis of the silicon hydride groups with the water in the reaction vessel. To compare two methods for determination of grafted Si-H groups concentration, selected samples (SiH-3 and SiH-8) were chosen as subject for iodometric titration. The obtained values were similar to those obtained with spectrophotometry (0.55±0.03 and 0.34±0.02 mmol/g of SiH groups respectively for SiH-3 and SiH-8 samples).

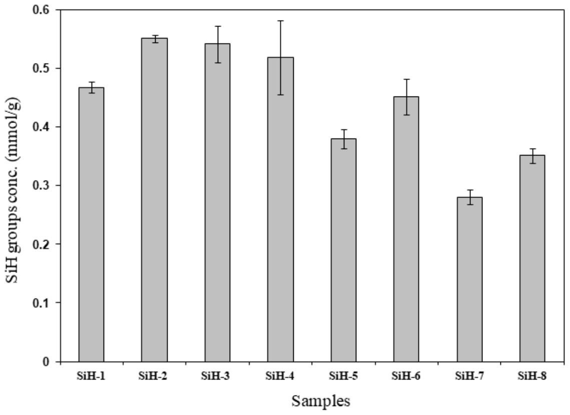

Fig. 11. Graph of SiH groups concentration (mmol/g) determined for synthesized samples using spectrophotometric determination with molybdenum blue ($n = 3$)

Since the SiH-8 sample, in our opinion, summarizes the most technological pathway of the hydrophilic-hydrophobic silica-hydride fabrication, further studies, in comparison with the pristine FS, were performed using this sample. By the results of spectrophotometric analysis, the quantified concentration of surface silicon hydride groups for the SiH-8 sample was in the range of 0.35±0.01 mmol/g, which is about 35 % of their quantity in the corresponding portion of the modifying agent used for hydridesilylation (1 mmol). This percentage may indicate the loss of ≡SiH groups both as a result of removal of residues of unreacted modifying agent and due to hydrolysis of these groups. Modification with triethoxysilane in a fluidized bed reactor reduces insignificantly the specific surface area of the initial FS – from 319 to 310 m^2/g. SEM photographs (Fig. 12) also confirm the minimal effect of surface modification on the structure and morphology of primary particles and agglomerates of fumed silica.

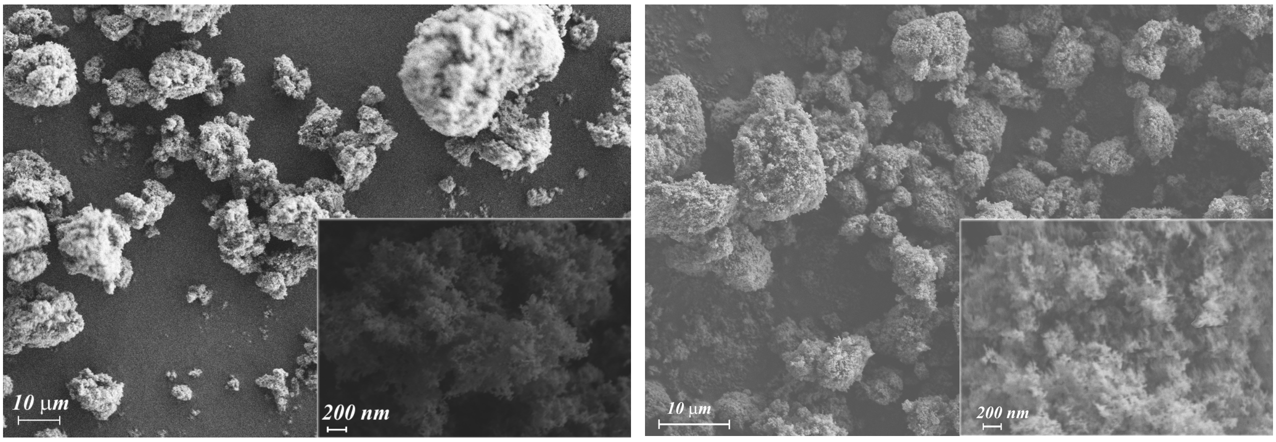

Fig. 12. SEM images of FS prior to modification (A-300, left) and after modification with TES in the presence of water (SiH-8, right)

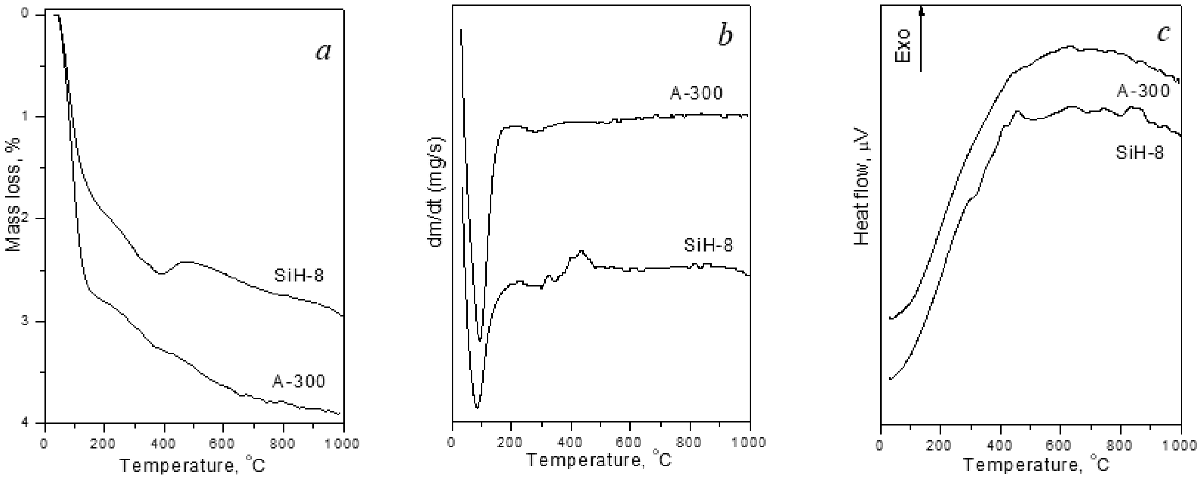

Fig. 13. TG (*a*), DTG (*b*) and DTA (*c*) curves of FS before (A-300) and after (SiH-8) modification with TES and water under fluidized bed conditions

The thermogravimetric analysis (TGA) was used to follow thermal degradation of silica samples under isothermal heating mode. In case of the initial FS (A-300), the TG curve have steady character of mass loss (Fig. 13 *a*) with one pronounced mass loss peak (25–150 °C) on the DTG curve (Fig. 13 *b*) with a maximum in the region of 100 °C, associated with the removal of physically sorbed water. This process is accompanied by a slight endo-effect on the DTA curve (Fig. 13 *c*). Subsequently, a slight weight loss can be caused by the removal of strongly bound water and water formed by condensation of surface silanol groups. The total weight loss is 3.9 %, of which about two thirds (2.7 %) occurred at temperatures up to 150 °C. The similarity in TGA curves in the same temperature range is observed for SiH-8 (Fig. 13) but the weight loss is twice less (1.7 %), which may be due to the hydrophobicity of grafted silicon hydride groups and residual ethoxy groups that do not act as centers of physical adsorption for water molecules when the sample is in contact with moist air. Another difference is an increase in sample weight in the temperature range 400–465 °C (Fig. 13 *a*). This process is accompanied by an exo-effect (Fig. 13 *b*) and is associated with the oxidation of silicon hydride groups ($\equiv SiH + 0.5O_2 \rightarrow \equiv SiOH$), which indirectly confirms their presence in the chemisorbed state on silica surface. The total weight loss is 3.2 %, of which about half (1.7 %) occurs at temperatures up to 150 °C and the difference between the total weight loss of both silica is about 1 %.

CONCLUSION

Fumed silica (A-300) undergone modification with triethoxysilane under fluidized bed conditions in order to prove a concept for such reaction and to reduce (avoid) the usage of solvent in the reaction. Control sample was synthesized via conventional wet-chemistry method. Parameters of the fluidized bed conditions, *i.e.* silica surface thermal pre-treatment, presence/absence of solvent or hydrolyzing agent were analyzed in respect to their effect on the contents of surface layer of obtained modified silicas.

Successful grafting of silicon hydride groups was confirmed with FTIR spectroscopy by appearance of characteristic band at about 2260 cm^{-1} for all samples under current investigation. It has been found that the degree of surface hydridesilylation for the majority of samples obtained under fluidized bed conditions without the water addition is about the same as that for control sample (about 0.55). The silica surface pre-treatment promotes more complete grafting of organic groups and reduction in hydroxyl groups, however it does not have noticeable influence on the final concentration of grafted SiH groups.

Chemical modification under fluidized bed conditions is suitable for obtaining HFS samples with high functional groups loading, with no need to use of solvents/acid catalysts, and with minimal impact on the morphology of fumed silica aggregates and its specific surface.

ACKNOWLEDGEMENT

The authors are grateful to Dr S.V. Snegir from the University of Konstanz (Germany) for the assistance in SEM investigations of initial and modified silica samples.

Спектроскопічне дослідження особливостей гідридсілілювання пірогенного кремнезему триетоксисиланом в умовах псевдозрідженого шару

П.О. Кузема, А.В. Коробейник, В.А. Тьортих

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, coralchance@gmail.com

Пірогенний кремнезем (ПК) знайшов широке застосування в промисловості завдяки різноманітним властивостям. За рахунок специфічності виробничого процесу він складається з дрібнодисперсних частинок і має розвинену питому поверхню, вкриту реакційно здатними силанольними групами, які доступні для реакцій хімічного прищеплення. Сферична форма частинок діоксиду кремнію та відсутність пористості забезпечують об'ємне заповнення простору структурою. Ці характеристики дозволяють використання пірогенних кремнеземів як носіїв з розвиненою поверхнею для каталізаторів, наночасток металів, органічних компонентів тощо. В даний час велика увага приділяється прищепленню на поверхні для поліпшення носіїв на основі діоксиду кремнію. Більшість реакцій в цьому напрямку проводиться в розчинах, що включає великі об'єми коштовних і токсичних розчинників, тоді як властивості кремнезему, що заповнює простір, сприяють реакціям в умовах псевдозрідженого шару.

У даному дослідженні пірогенний діоксид кремнію (А-300) був об'єктом гідридсилілювання триетоксисиланом (ТЕС) в умовах псевдозрідженого шару. У запропонованому авторами синтезі не було застосовано або було витрачено незначну кількість (1.00 мас. % від кількості, що використовується в типовому методі модифікування) розчинника, лише для розчинення модифікатора та каталізу прищеплення силану. Масове співвідношення кремнезем/ТЕС підтримували постійним, інші умови, наприклад, наявність *розчинника/каталізатора, попередня обробка поверхні, додаткова обробка водою та режим нагрівання в киплячому шарі, варіювали. Аналіз ІЧ спектрів виявив взаємодію між етоксильними групами молекул TEC та силанольними групами поверхні, а також продемонстрував вплив умов модифікування на склад гідридсилільного покриття.*

Результати ІЧ спектроскопічних досліджень підтвердили наявність на поверхні модифікованого кремнезему прищеплених кремнійгідридних груп, а також етоксильних та/або силанольних груп – як вихідних, так і утворених в результаті гідролізу етокси-груп. Титриметричний та спектрофотометричний аналіз показав, що в залежності від умов синтезу концентрація прищеплених SiH груп в усіх випадках модифікування у псевдозрідженому шарі коливалась у межах приблизно 0.28–0.55 ммоль/г. Обговорено також важливі аспекти запропонованого методу модифікування у псевдозрідженому шарі, а саме – наявність розчинника та/або гідролізуючого агента, режим нагрівання та вплив попередньої обробки зразка діоксиду кремнію.

Ключові слова: *кремнезем, модифікування поверхні, кремнійгідридні групи, псевдозріджений шар*

REFERENCES

1. Barthel H., Rösch L., Weis J. Fumed Silica – Production, Properties, and Applications. In: *Organosilicon Chemistry II*. (Weinheim :VCH Verlagsgesellschaft mbH, 1995).
2. Chuiko A.A. *Medicinal chemistry and clinical application of silicon dioxide*. (Kyiv: Naukova Dumka, 2003). [in Russian].
3. Pratsinis S.E. Flame aerosol synthesis of ceramic powders. *Prog. Energy Combust. Sci.* 1998. **24**(3): 197.
4. Korobeinyk A.V., Whitby R.D.L., Mikhalovsky S.V., Inglezakis V.J. In situ production of high purity noble metal nanoparticles on fumed silica and catalytic activity towards 2-nitrophenol reduction. *J. Phys. Chem. Solids*. 2019. **127**: 28.
5. Budnyak T.M., Błachnio M., Slabon A., Jaworski A., Tertykh V.A., Deryło-Marczewska A., Marczewski A.W. Chitosan Deposited onto Fumed Silica Surface as Sustainable Hybrid Biosorbent for Acid Orange 8 Dye Capture: Effect of Temperature in Adsorption Equilibrium and Kinetics. *J. Phys. Chem. C.* 2020. **124**(28): 15312.
6. Ivashchenko N.A., Katok K., Tertykh V., Yanishpolskii V., Khainakov S. Silica with grafted silicon hydride groups and its application for preparation of palladium nanoparticles. *Int. J. Nanoparticles*. 2011. **4**(4): 350.
7. Bolbukh Y.N., Mamunya Y.P., Tertykh V.A. Thermomechanical properties of polymeric composites based on 2-hydroxyethylmethacrylate and fumed silicas. *J. Therm. Anal. Calorim.*. 2005. **81**(1): 15.
8. Kuzema P.O., Starokadomsky D.L., Tkachenko O.O., Tertykh V.A. Reinforcement of epoxy polymers with hydridesilylated fumed silica. *Him. Fiz. Tehnol. Poverhni*. 2020. **11**(4): 484.
9. Bolbukh, Y.M., Kuzema P.O., Tertykh V.A., Gawdzik B. Effect of Surface Hydride, Vinyl, and Methyl Groups on Thermal Stability of Modified Silica-Divinylbenzene-Di(Methacryloyloxymethyl)Naphthalene Composites. *Int. J. Polym. Mater. Polym. Biomater.* 2007. **56**(8): 803.
10. Qian Ch., Sun W., Hung D.L.H., Qiu Ch., Makaremi M., Kumar S.G.H., Wan L., Ghoussoub M., Wood T.E., Xia M., Tountas A.A., Li Y.F., Wang L., Dong Y., Gourevich I., Singh Ch.V., Ozin G.A. Catalytic CO_2 reduction by palladium-decorated silicon–hydride nanosheets. *Nat. Catal.* 2019. **2**(1): 46.
11. Yates J.G., Lettieri P. Fluidized-Bed Scaling. In: *Fluidized-Bed Reactors: Processes and Operating Conditions. Particle Technology Series.* (Cham: Springer, 2016).
12. Tertykh V., Yanishpolskii V., Bolbukh Y. Synthesis and characterization of functional chemically modified silica fillers. *Macromol. Symp.* 2003. **194**(1): 141.
13. Swihart M.T., Girshick S.L. Thermochemistry and Kinetics of Silicon Hydride Cluster Formation during Thermal Decomposition of Silane. *J. Phys. Chem. B.* 1999. **103**(1): 64.
14. Gates S.M., Kunz R.R., Greenlief C.M. Silicon hydride etch products from the reaction of atomic hydrogen with Si(100). *Surf. Sci.*, 1989. **207**(2–3): 364.
15. Bhandarkar U.V. Modelling of silicon hydride clustering in a low-pressure silane plasma. *J. Phys. D: Appl. Phys.* 2000. **33**(21): 2731.
16. Staszczuk P., Jaroniec M., Gilpin R.K. Thermoanalytical studies of water films on porous silicas at subambient and elevated temperatures. *Thermochim. Acta.* 1996. **287**(2): 225.
17. Müller A.C., Serain C. Soluble molybdenum blues – “des Pudels Kern”. *Acc. Chem. Res.* 2000. **33**(1): 2.

18. Tsigdinos G.A., Chen H.Y., Streusand B.J. Molybdate solutions for catalyst preparation. Stability, adsorption properties, and characterization. *Ind. Eng. Chem. Prod. Res. Dev.* 1981. **20**(4): 619.
19. Morrow B.A., McFarlan A.J. Surface vibrational modes of silanol groups on silica. *J. Phys. Chem.* 1992. **96**(3): 1395.

Received 22.07.2021, accepted 01.12.2021