

Polymerization of Vinyl Monomers on the High Disperse Aluminum-Containing Silica

by **S.I. Levytska, A.G. Grebenyuk and V.V. Brei**

*Institute of Surface Chemistry of the National Academy of Sciences,
Generala Naumova str., 17, 03164 Kyiv, Ukraine
E-mail: brei@alfacom.net*

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The interaction of vinyl monomers (styrene, butyl vinyl ether, N-vinylpyrrolidinone, vinyltrimethylsilane, methyl acrylate, vinyl acetate, and vinylacetonitrile) vapours with alumino-aerosil surface has been studied by IR spectroscopy, thermal gravimetry, field ionization mass-spectrometry, and by quantum chemical simulations. The Brønsted acidic sites of the oxide ($H_0 \leq -3.0$) were found to be capable to initiate an oligomerization of butyl-vinyl ether, styrene and N-vinylpyrrolidinone, whereas the monomers containing electron acceptor substituents (methyl acrylate, vinyl acetate, and vinylacetonitrile) are sorbed only in a physical way. The method of vapour phase oligomerization at temperatures 30–120°C has been shown to be a suitable way to produce disperse composite materials with a great content of organic matter (40–60 wt. %). Experimental and calculated absorption spectra support the idea on the formation of both monomeric and oligomeric protonated species due to adsorption of vinyl monomers on the surface of aluminum-containing silica unlike on that of pure silica.

Key words: polymerization, vinyl monomer, silica, composite materials, quantum chemistry

In order to produce mineral fillers with hydrophobic properties, a chemical modification of their surfaces is applied, as a rule, with organic and element-organic compounds, in particular, with organosilicones [1]. An examination of vapour phase oligomerization of vinyl monomers on disperse oxide surfaces is of interest as a perspective method of producing such materials. As a rule, the initiation of the polymerization process of adsorbed vinyl monomers needs an additional introduction of catalysts, mostly peroxo compounds [1,2], application of UV- or γ -irradiation, or mechano-chemical activation of oxide surface [3]. The investigation of the processes of cationic polymerization of vinyl monomers with participation of oxide surface acid sites was paid considerably less attention [4]. Olefins are known to be capable to oligomerize on the surface of acid aluminosilicate catalysts [5–8]. This is an undesirable factor in such processes, as isobutane alkylation with isobutene or catalytical cracking, because it results in diminishing the catalytical activity, due to coke formation. Nevertheless, the oligomerization of vinyl monomers on the surface of high disperse pyrogenic aluminum-containing silica (that is characterized by a moderate Brønsted acidity [9]) can be a perspective process for production of modified fillers. This paper includes data on the capability of vinyl monomers with different functional groups to oligomerize with participation of B-sites of alumino-aerosil surface.

EXPERIMENTAL

Synthesis. The oligomerization processes were studied on alumino-aerosil samples (AAS) produced at Kalush experimental plant of the Institute of Surface Chemistry, National Academy of Sciences of Ukraine, *via* joint vapour hydrolysis of SiCl_4 and AlCl_3 within air-hydrogen flame (specific area of 160–65 m^2/g , Al_2O_3 contents 3–6 wt. %). The following reactants served as monomers: butyl vinyl ether (98%, Fluka), vinyl acetate (99%, Merck), vinylacetonitrile (98%, Aldrich), N-vinylpyrrolidinone (99%, Sigma-Aldrich), methyl acrylate (99%, Sigma-Aldrich), styrene (98%, Aldrich). The monomers were just used in experiments after low-pressure (10–15 Torr) distillation. A vacuum apparatus was used for the examination of monomer interaction with AAS surface (a quartz cell with fluorite windows was used as a reactor). The AAS samples were calcined within oxygen current at 400°C for 30 minutes in order to remove admixtures of sorbed organic substances, then thermoevacuated for 15 minutes at 400°C (10^{-3} Torr) for removal of physically sorbed water and cooled in vacuum to room temperature. After that monomers were adsorbed from gas phase. When monomers interacted with AAS surface, IR spectra were recorded at different temperatures (20–200°C).

In order to determine the temperature of the polymerization process of the monomers studied, alumino-aerosil powder was packed down in platinum crucible, calcined in oxygen stream at 400°C for 30 minutes and cooled in argon to room temperature; then the respective monomer was added and thermogram recording just began. In order to be compared, thermograms of respective polymers were recorded as well as those of alumino-aerosil with individual polymers adsorbed from the solutions onto its surface.

The synthesis of the samples of modified AAS was carried out in a rotation reactor in argon atmosphere. A sample of AAS calcined in oxygen current at 400°C (30 minutes) was cooled in argon for 30 minutes, then the respective monomer was added at a rate of less than 1 ml/min. The synthesis was carried out during 1 hour at the temperature selected for each monomer under permanent stirring. After that argon was blown through the reactor for 30 minutes at the reaction temperature, in order to remove monomer residues.

Characterization methods. Total acidity of the oxides was determined by the method of reverse titration with use of benzene solution of *n*-butylamine and bromthymol blue as an indicator [10]. The strength of acidic sites was estimated due to the change in color of respective Hammett indicators in benzene solution [5].

IR spectra of the samples prepared as thin (mass of 15–20 mg, size of 25×8 mm) AAS pills were recorded on a Perkin-Elmer-325M spectrophotometer using a quartz cell with fluorite windows. Different thermal and thermogravimetric analyses (DTGA) were performed with a Q-1500D (MOM, Budapest, Hungary) derivatograph between of 20–1000°C. Field mass-spectra of modified AAS samples were recorded on a MI-1201 mass-spectrometer (“Selmi”, Sumy, Ukraine). Molecular masses of extracted oligomers were determined exclusion-liquid chromatography (a DuPont-8800 chromatograph). Electron spectra of diffuse reflectance of modified AAS were recorded on a Specord M-40 spectrophotometer (Carl Zeiss, Jena, Germany) ($R = R_{\text{sample}}/R_{\text{MgO}}$).

Quantum chemical calculations. Simulation of equilibrium geometry and energy of the adsorption complexes of vinyl monomers and their protonated forms on the surface of aluminum-containing silica was performed by SCF MO LCAO method within the semi-empirical MNDO approximation [11] by the program [12], received from the authors. Silica surface was simulated by a globular cluster model of $\text{Si}_4\text{O}_6(\text{OH})_{14}$ [13] and that of aluminum-containing silica – by that of $\text{AlSi}_3\text{O}_5(\text{OH})_5$. Such a way of constructing models allowed to eliminate frontier conditions and at the same time to provide an appropriate equality of the angles of Si–O–Al and Si–O(H)–Al what had a substantial importance for the correct description of the process of proton transfer from the surface to adsorbed molecule under conditions of total geometry optimization of the adsorption complex.

Singlet-singlet transitions of molecules of styrene, N-vinylpyrrolidinone, and of their dimers, butyl vinyl ether, and of their protonated forms were calculated within π -electron approximation of Pariser-Parr-Pople with taking into account the effect of interaction of all the single excited configurations [14], by help of the PPP program, firstly written by L.I. Savransky (T.G. Shevchenko Kyiv National University), and then edited and designed for MS DOS by one of the authors (A.G. Grebenyuk) and E.V.

Aksenenko (A.V. Dumansky Institute of Colloid Chemistry and Chemistry of Water, National Academy of Sciences of Ukraine).

RESULTS AND DISCUSSION

A hypothesis served as a foundation of the study that Brønsted (B) sites of AAS surface are capable to initiate the process of vinyl monomer oligomerization *via* a cationic mechanism. The data on the B-site distribution for their strength are given in Fig. 1. It was found, that there are sites on the surface of AAS investigated characterized by $H_0 \leq -3.0$, what is equal to the strength of 48% solution of sulfuric acid. The part of B-sites within the interval of $+3.3 \leq H_0 \leq -3.0$ is about 23%.

A shift of the absorption band of stretching O–H vibrations of silanol groups from 3750 cm^{-1} to $3500\text{--}3300 \text{ cm}^{-1}$ is observed in the IR spectra of thermoevacuated AAS after its contact with vapours of butyl vinyl ether, styrene, and N-vinylpyrrolidone, as well as an appearance of intensive bands of stretching and bending C–H vibrations and a considerable decrease in intensity of the C=C stretching vibrations ($\nu_{\text{C}=\text{C}}$). This can testify the participation of the AAS surface OH-groups in the sorption of monomers given and in the run of oligomerization process. Fig. 2 presents the IR spectra of aluminoaerosil after its contact with styrene vapour. The disappearance of the $\nu_{\text{C}=\text{C}}$ band at 1627 cm^{-1} and the appearance of the bands of stretching C–H vibrations in the region of $2900\text{--}2800 \text{ cm}^{-1}$ (characteristic of polystyrene) testifies the formation of styrene oligomers on the aluminoaerosil surface. IR spectra of oligomers extracted from the AAS surface coincide with those of respective polymers, what is illustrated in Fig. 3, styrene being taken as an example. As it is seen, both the spectra include the absorption bands at 960 and 1070 cm^{-1} , peculiar to heterotactic polystyrene. The extracted modifier itself is a high-viscous, transparent yellowish mass.

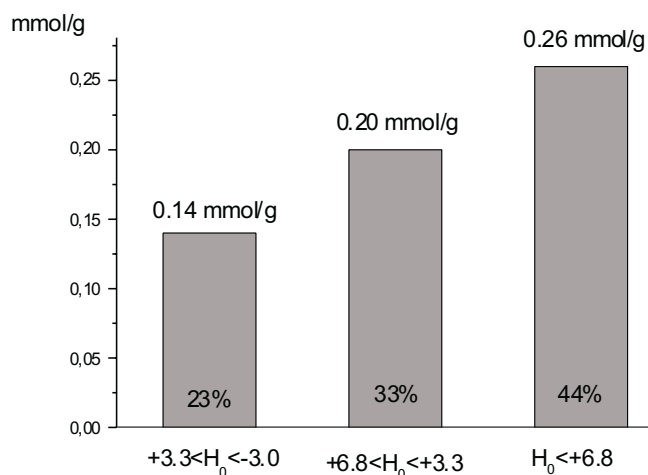


Figure 1. The distribution of B-sites for their strength on aluminoaerosil surface.

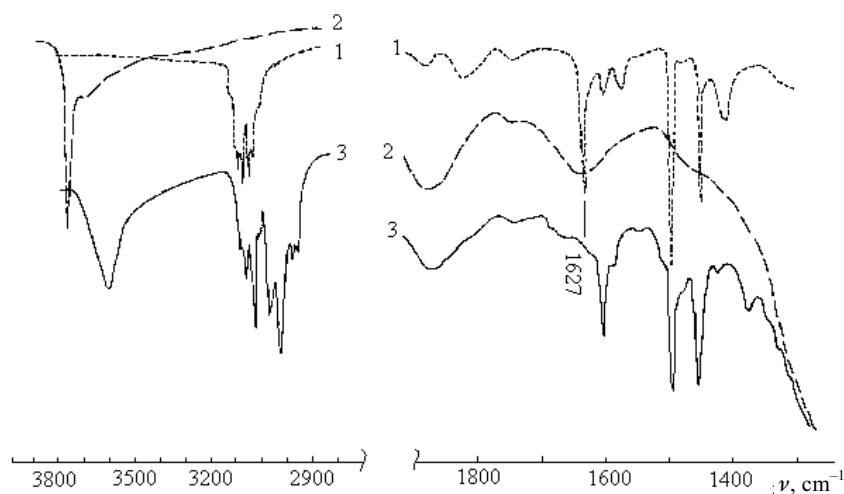


Figure 2. IR spectra of aluminosilica evacuated at 400°C (2), after contact with styrene vapour at 80°C (3); spectrum of styrene monomer (1).

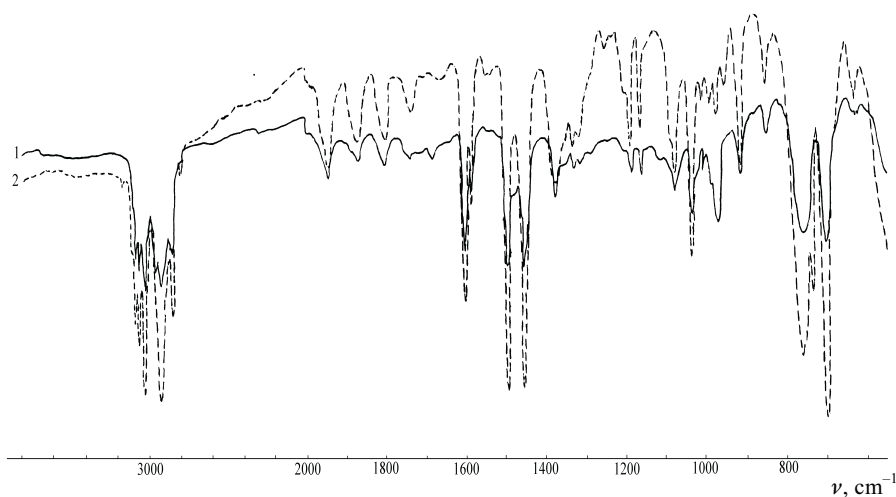


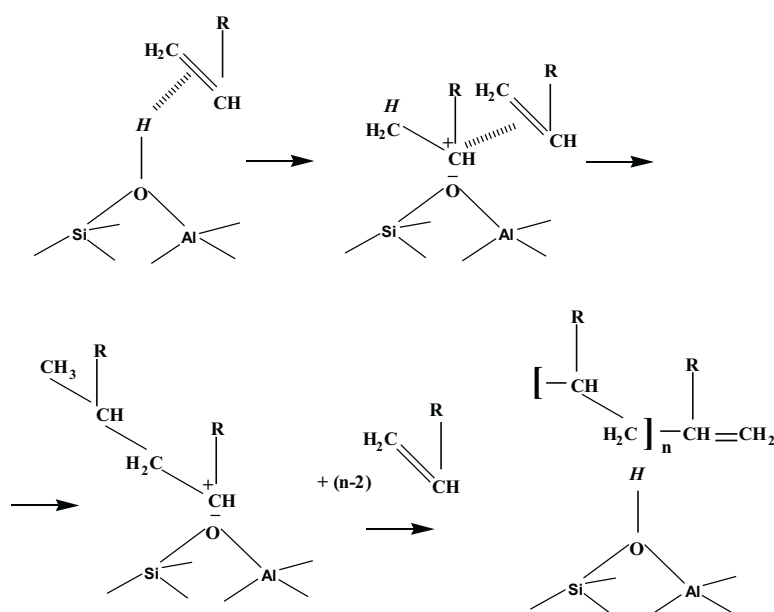
Figure 3. IR spectra of polystyrene extracted from modified AAS surface (80°C, 1 mmol/g, 1 h) (1) and of polystyrene film (Aldrich, molecular mass = 280000) (2).

It should be noted, that in cases of the contact of AAS with vapours of vinylacetonitrile, vinyl acetate, and methyl acrylate within the temperature interval of 30–150°C, there were no spectral manifestation in the IR spectra of aluminosilica mentioned above (Fig. 2). Thus, as a rule, after evacuation of the samples at 100°C, the band of stretching C–H vibrations (2900–2800 cm⁻¹) was not registered practically, *i.e.* only adsorption, not oligomerization, of these monomers was observed. A cationic-type polymerization is not characteristic for the monomers mentioned [4], what is explained by a considerable reduction of electron density at the vinyl group, due to the electron acceptor –CN and –OC(O)-R groups.

A comparison of the DTGA curves of the systems studied (aluminoaerosil + monomer) with those of the compositions (aluminoaerosil + polymers added) and of initial polymers gives a reason to assign the first exothermic peaks of the TG curves for the system (aluminoaerosil + monomer) to the heat effects of polymerization [15]. For the system (AAS + N-vinylpyrrolidinone) such a maximum is observed at 125°C, whereas that for the system (AAS + styrene) it appears at 80°C. When n-butyl vinyl ether reacts with AAS, no exothermic maximum at low temperatures is present, but there are such effects near the temperature region of oligomer destruction. In this case one can believe that the polymerization process occurs even at room temperature. The DTGA data allowed us to choose the temperature conditions of the sample synthesis in rotational apparatus in an inert gas atmosphere. The optimal temperature for N-vinylpyrrolidinone oligomerization on aluminoaerosil surface is between 110–120°C, that for styrene being of 70–80°C and for n-butyl vinyl ether of 20–30°C.

The formation of the surface oligomers of butyl vinyl ether, styrene, and N-vinylpyrrolidinone were supported by the field mass-spectra of the modified AAS samples (Fig. 4). Thus, styrene oligomers with chain length of up to 14 monomer units were observed. The styrene polymer formed on AAS surface was extracted with chloroform and examined by the method of exclusion-liquid chromatography. Its average molecular mass appeared to be of 1267 a.u.m., and a molecular mass distribution was narrow enough: a ratio of $M_w:M_n$ was of 1.128. The value of molecular mass determined by chromatographic method coincides with the data of mass-spectrometry analysis.

The results described suggest that there is observed an oligomerization on AAS surface of such vinyl monomers as butyl vinyl ether, styrene and N-vinylpyrrolidinone. This process passes with participation of aluminoaerosil surface B-sites, due to a probable scheme:



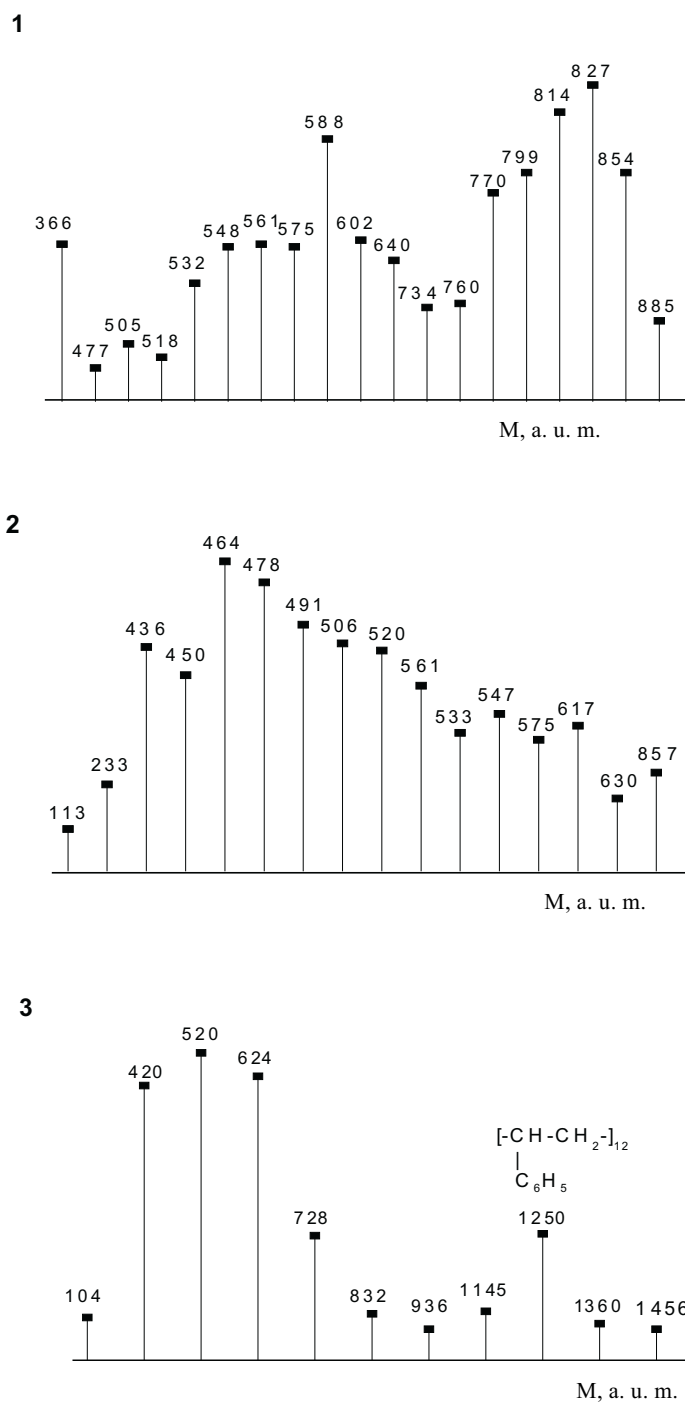
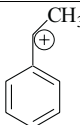
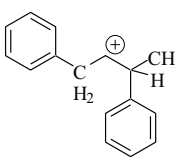
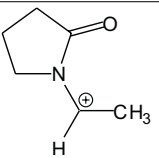
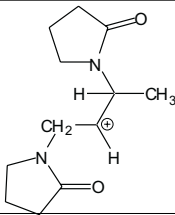
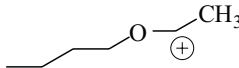


Figure 4. Field mass-spectra of aluminoaerosil modified with butyl vinyl ether, $T_{des} = 140^\circ\text{C}$ (1), N-vinylpyrrolidinone, $T_{des} = 140^\circ\text{C}$ (2), styrene, $T_{des} = 140^\circ\text{C}$ (3).

There are formed relatively stable carbenium ions of butyl vinyl ether, what is testified by a yellowish-brown color of the sample, vanishing after a contact with air. In the electron spectra of diffuse reflectance for the modified samples this effect corresponds to the appearing of new bands with maxima within the visible region (see Table 1). When styrene and N-vinylpyrrolidinone interact with the zeolite HZSM-5 sample (Si/Al = 17) that has B-sites with $H_0 \leq -5.6$, carbenium ions are also formed and kept stable in air for a continuous time. Nevertheless, no oligomer formation is observed under conditions given on the zeolite surface, due to steric difficulties caused by its porous structure. It should be mentioned that no oligomer compound is observed, when these vinyl monomers are adsorbed on Degussa-OX-50 aerosil that does not contain acid sites with $H_0 \geq +4.8$.

Table 1. Calculated and experimental spectra of protonated forms of styrene, N-vinylpyrrolidinone, butyl vinyl ether, and their dimers (λ_{\max} – absorption maximum).

| Structure | Calculation | | Experiment | |
|---|-----------------------|------------|-----------------------|-----------------------|
| | λ_{\max} , nm | Extinction | λ_{\max} , nm | Relative intensity, % |
|  | 457 | 17000 | 415 | 29 |
| | 299 | 23000 | 350 | 26 |
| | 219 | 2600 | 296 | 43 |
| | 210 | 6600 | 286 | 48 |
|  | 757 | 1600 | 850 | 35 |
| | 598 | 1 | 600 | 63 |
| | 416 | 1900 | 555 | 100 |
| | 322 | 15000 | 520 | 82 |
| | 273 | 4500 | 415 | 70 |
| | 220 | 2200 | | |
|  | 417 | 2420 | 418 | 17 |
| | 325 | 9810 | 288 | 37 |
| | | 1430 | 248 | 94 |
| | | 3880 | 244 | 94.8 |
| | | 8710 | 240 | 94.5 |
| | | 15400 | 236 | 94 |
|  | 500 | 331 | 550 | 18 |
| | 412 | 473 | 515 | 16 |
| | 354 | 17700 | 418 | 17 |
| | 304 | 8940 | 390 | 19.5 |
| | 254 | 7770 | 288 | 37 |
| | | | 248 | 94 |
| | | 244 | 94.8 | |
|  | 440 | 2100 | 440 | 50 |
| | 282 | 4800 | 419 | 57 |
| | 207 | 6000 | 390 | 63 |
| | | | 365 | 68 |
| | | | 328 | 80 |
| | | | 314 | 77 |
| | | | 283 | 80 |
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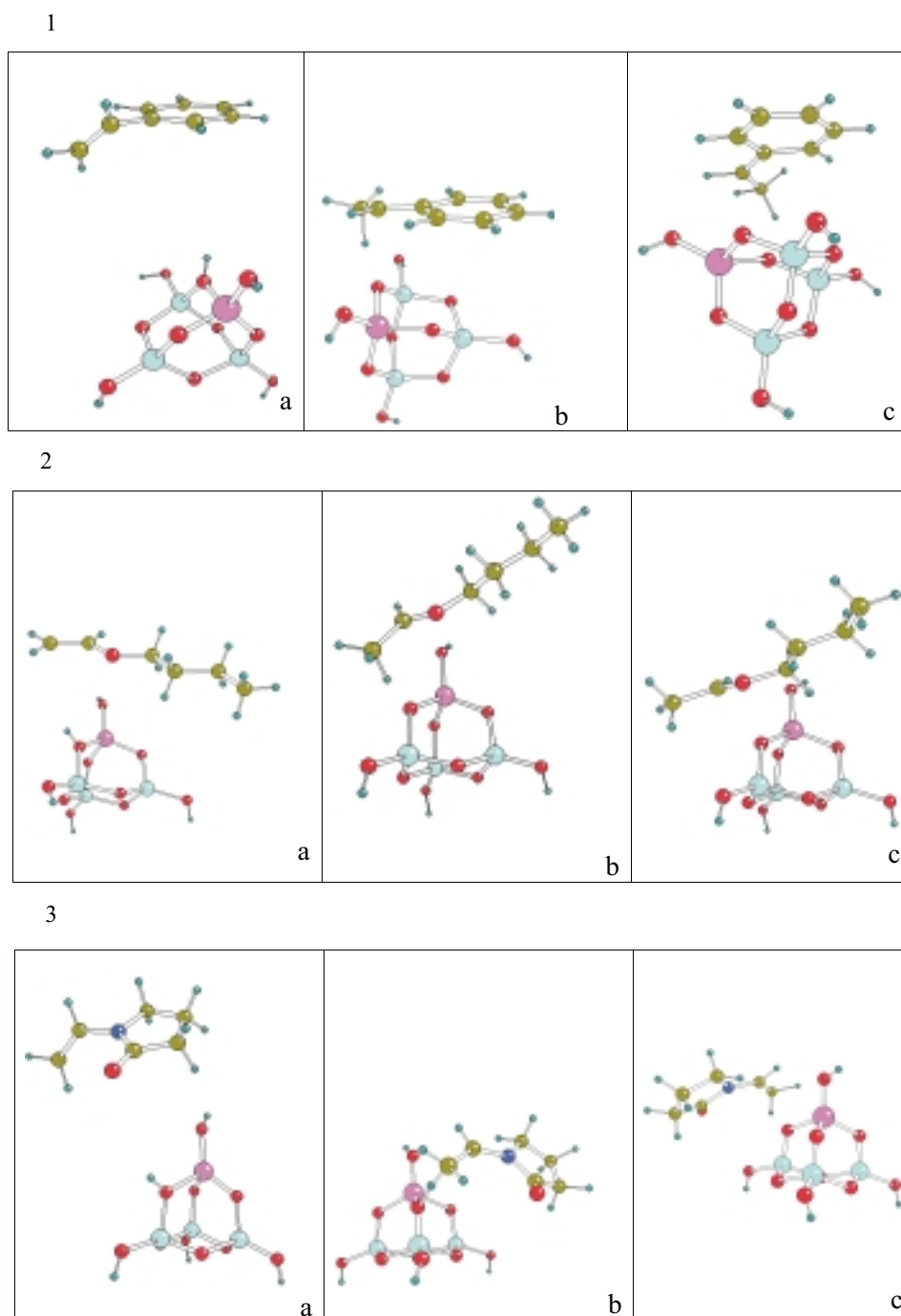


Figure 5. Adsorption forms of styrene (1), butyl vinyl ether (2), and N-vinylpyrrolidinone (3) on the surface of aluminum-containing silica (a – molecular sorption, b – transition state, c – ionic pair).

As for N-vinylpyrrolidinone (110°C, 1 hour), up to 14 mmol of monomer per 1 g AAS is oligomerized what corresponds to the content of organic matter in modified oxide of 60 wt. %. For n-butyl vinyl ether (25°C) this value is of 47 wt. % (9 mmol/g), and for styrene (80°C) – 42 wt. % (7 mmol/g). The velocity of cationic polymerization in the liquid phase is known to increase with lowering temperature [4]. The decrease in polymerization temperature on AAS surface (from 80°C to –10°C for styrene and from 25°C to –10°C for n-butyl vinyl ether) results in a decrease of the mass of oligomers formed (for 43 wt. % and 13 wt. % respectively), what testifies the difference in cationic polymerization of vinyl monomers in liquid phase and on oxide surface.

In order to justify the experimental results obtained, quantum chemical calculations were carried out on the electron spectra of the carbocations obtained as well as a comparative theoretical analysis was made of the adsorption forms of butyl vinyl ether, styrene, and N-vinylpyrrolidinone molecules on the surface of aluminum-containing silica. The results of the calculations of electron spectra are given in Table 1. It follows from the data given, that the change in colour of n-butyl vinyl ether, due to protonation, can be basically described without use of the idea on oligomerization, whereas long-waves absorption bands of styrene and N-vinylpyrrolidinone can be explained by oligomer formation. Differences between calculated and experimental spectra are conditioned by both fault of the calculation method (about 15–20 nm) and spectral shift, due to electrostatic effect of the adsorbent matrix [16] and changes in molecular conformations, as well as manifestations of the vibration structure of absorption bands.

We made an attempt by quantum chemical simulation to fix a connection between surface acid-base properties of pure and aluminum-containing silica, from one hand, and to verify the opportunity of ionization (carbocation formation) of styrene, n-butyl vinyl ether, and N-vinylpyrrolidinone, from the other hand.

The equilibrium geometry of the structures examined is given in Fig. 5. On the surface of aluminum-containing silica styrene, capable to be sorbed in a molecular way (adsorption enthalpy is of –1.6 kcal/mol); then, a proton transition can take place from the bridge Si–OH–Al group to styrene molecule with formation of a carbocation, what can be a start for ionic polymerization. On the contrary, pure silica surface cannot ionize the adsorbed styrene molecules: when started from an ion pair, the energy optimization procedure results in a merely grafted alkoxy group.

It should be noted that the ionic pair is separated from the molecular state by a potential barrier (of about 10 kcal/mol; in the transition state proton moves away from the bridge oxygen atom for 155 nm), but has a higher value of the formation enthalpy (for 59.6 kcal/mol). This fact means, that only a small part of styrene molecules can transform into the ionic form. The thermodynamic disadvantage of the ionic pair formation, following from our calculations, can be explained by both faults of parametrization of the calculation method used and a relatively small size of the cluster simulated for the surface (insufficient for energy stabilization of the cation [17]). Moreover, the proton donor capability of the surface of aluminosilicate catalysts considerably depends on their composition and geometrical structure [18], in particular, on the value of Si–O–Al angle.

When adsorbed, butyl vinyl ether performs a similar behaviour. Besides molecular adsorption form (adsorption enthalpy is of -0.9 kcal/mol), an ionic pair can be formed (a potential barrier of 61.9 kcal/mol has to be overcome) that has the higher energy for 48.2 kcal/mol. N-vinylpyrrolidinone on aluminosilica can also be ionized, and the molecular form of adsorption (adsorption enthalpy is of 0.8 kcal/mol) is separated from ionic one by a potential barrier of 51.4 kcal/mol and is energetically more profitable than the latter for 45.2 kcal/mol. Thus, when compared, the experimental and calculated absorption spectra support the idea on the formation of both monomeric and oligomeric protonated species, due to adsorption of vinyl monomers on the surface of aluminum-containing silica.

CONCLUSIONS

It has been found that an oligomerization occurs on the surface of AAS, unlike on that of pure silica, of vinyl monomers with electron donor substituents (butyl vinyl ether, N-vinylpyrrolidinone, styrene). The activity of these monomers in the process of cationic polymerization initiated by the oxide surface decreases in the sequence: butyl vinyl ether, styrene, N-vinylpyrrolidinone. There exists an opportunity to produce composite materials with a high content of organic matter (40–60 wt. %) by the method of vapour phase oligomerization of monomers on aluminosilica at moderate temperature (30–120°C).

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