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THE SOL-GEL METHOD FOR PREPARATION OF POLYSILOXANE XEROGELS CONTAINING CARBOXYLIC FUNCTIONALITY

O.A. Dudarko[1]*, Yu.L. Zub[1], M. Jaroniec[2], M.G.White[3], Qihua Yang[4]

[1]O.O. Chuiko Institute of Surface Chemistry, NAS of Ukraine,
17, General Naumov Str., Kyiv 03164 Ukraine
[2]Department of Chemistry, Kent State University, Kent, OH 44242, USA
[3]The Dave C. Swalm School of Chemical Engineering, Mississippi State University,
330 Swalm Chemical Engineering Building, Mississippi State, MS 39762, USA
[4]Dalian Institute of Chemical Physics, 457 Zhongshan Road, Dalian, 116023, PR of China

A procedure has been developed for synthesis of new polysiloxane xerogels with propionic and butyric acid-type groups. The procedure is based on the sol-gel method and involves the conversion of 2-cyanoethyltriethoxysilane (or 4-(triethoxysilyl)butyronitrile) to an ester with its subsequent hydrolytic polycondensation reaction. The conversion proceeds under mild conditions and requires a gaseous HCl and the presence of tetraethoxysilane, $Si(OC_2H_5)_4$. The IR and ^{13}C CP/MAS NMR spectroscopy studies showed that some carboxylic groups were converted to an ester as $\equiv Si(CH_2)_{2\ or\ 3}C(O)OC_2H_5$ using this procedure. Nitrogen adsorption analysis indicated that the resulting samples possessed pores on the borderline between micro- and mesopores (average micropore width was equal to 2.1-2.2 nm) and exhibited high BET specific surface areas (370-680 m^2/g).

Introduction

In response to technological challenges of adsorption, chromatography, analytical chemistry, sensor technology, etc., the chemistry of modified silicas has made a substantial progress over the last two decades [1–5]. Up to now, the grafting of organosilanes or other organic compounds on silica continues to be one of the promising methods for the synthesis of new materials. At the same time, while silicas modified by amine, thiol or phosphine groups have been often reported, these with carboxylic functionalities have attracted much less attention [6–9]. It should be noted that the silicas with immobilized carboxylic acids (often aromatic or high molecular weight acids) found the use in separation processes [10, 11], medicine-related preparations [12, 13], and in heterogeneous catalysis of alkene epoxidation [14]. But the presence of long alkyl chains in the surface layer imparts hydrophobic properties of these materials. Besides, the weight fraction of functional groups is, as a rule, small.

It seems that the disadvantages indicated above may be avoided by applying the sol-gel method to the synthesis of functionalized polysiloxane xerogels (FPX) with carboxylic functionality. This method allows one to vary reaction conditions [15]. For example, it is possible to vary the ratio of alkoxysilanes and, thereby, to increase the content of functional groups on the surface. At the same time, the control of some other conditions of the synthesis allows one to synthesize materials with high sorption capacity and well-developed porous structure of desired pore sizes and surface functionality. Nevertheless, a few attempts have been made to synthesize carboxyl-containing xerogels.

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*To whom correspondence should be addressed. O.A.Dudarko, O.O.Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str., Kyiv 03164 Ukraine; e-mail: dudarko@bigmir.net

One of such attempts was made by using the hydrolytic polycondensation of organosilicon monomers such as trichlorosilylbutiryl chloride or silyl ester of triethoxysilylbutyric acid [16]. However, the formed insoluble polymers swell easily. Besides, they are thermally resistant up to 200°C only. Thus, they do not have distinct advantages in comparison to simple organic cation exchangers. The same refers to the product of copolymerisation of acrylic acid and alyltriethoxysilane [17]. There was an attempt to carry out hydrolytic polycondensation of $(CH_3O)_3Si(CH_2)_2SCH_2COOSi(CH_3)_3$ but it was unsuccessful neither under acidic nor basic conditions [18]. Therefore, the synthesis of polysiloxane xerogels reported in [18] employed $(CH_3O)_3Si(CH_2)_2SCH_2COOH$ without further cleaning. This way in both acidic (yield 69%) and alkaline (yield 21%) medium appropriate polyorganosilsesquioxanes were formed. A successful attempt to synthesize carboxyl-containing xerogel by saponification of nitryl groups under quite strong conditions (which can cause a loss of the part of these groups) has been reported in [19]. The aim of the present work was to develop a sol-gel method for the synthesis of carboxyl-containing polysiloxane xerogels by using the approach that has been described in [20], and to study their properties. This method was developed for the FPX materials containing carboxylic groups originated from propionic, $–(CH_2)_2COOH$ and butyric, $–(CH_2)_3COOH$ acids [21].

Experimental

The starting materials were tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS), 2-cyanoethyltriethoxysilane $(C_2H_5O)_3Si(CH_2)_2CN$ (CETES), 4-(triethoxysilyl)butyronitrile $(C_2H_5O)_3Si(CH_2)_3CN$ (CPTES), and catalyst $(n\text{-}C_4H_9)_2Sn(CH_3COO)_2$ (Aldrich, 98%). The solvent was 96 % or absolute ethanol produced by the same company.

Synthesis of FPX with 2-cyanoethyl groups (sample A). 0.1 mol (22.3 cm^3) of TEOS and 0.05 mol (11.1 cm^3) of CETES were added to 20 cm^3 of absolute ethanol at room temperature. Next, 1 g (0.76 cm^3) of $(n\text{-}C_4H_9)_2Sn(CH_3COO)_2$ and 0.264 mol (4.75 cm^3) of H_2O were added successfully to the above mentioned alkoxysilane solution continuously mixed with a magnetic stirrer. The mixture was heated up to 80 °C and kept at room temperature for 96 h. The formed gel was dried under vacuum at 105 ºC for 6 h. The resulting xerogel was washed with water up to pH 6.5 and repeatedly dried giving the white product (about 13.6 g).

Synthesis of FPX with simultaneous saponification of nitrile groups (B). In a flask 2 cm^3 of acid solution (anhydrous acetic acid, concentrated sulfuric acid, and water with the volume ratio of $CH_3COOH:H_2SO_4:H_2O = 1:1:3$) was added drop-by-drop to the mixture of 0.01 mol CETES and 0.02 mol TEOS under magnetic stirring. The product formed at room temperature for 30 min was a white gel. The gel prepared during 96 h was similar to those described above.

Synthesis of propionic acid-containing FPX (C). 0.05 mol of CETES and 0.2 mol of TEOS were placed in a three-neck reactor. A gaseous HCl was bubbling through the mixture under continuous stirring with a magnetic stirrer for 3 h and next 50 cm^3 of 96 % ethanol was added drop-by-drop to this mixture. Next, 125 cm^3 of 0.02 % solution of hydrochloric acid was gradually added during 18 h followed by heating the mixture at 80 °C for 40 min. The product formed was a white gel, which was dried and washed as described in the previous syntheses, i.e., dried under vacuum at 105 ºC for 6 h (sample C). The white product yield was equal to 19.6 g. The xerogel (sample D) was dried at 105 ºC under the atmosphere pressure. The xerogel sample E (yield 13.0 g) was prepared by using the molar ratio of TEOS/CETES = 2:1 and the recipe analogous to that used for the sample C.

Synthesis of buturic acid-containing FPX (F). The above described method of synthesis of the sample C was employed to obtain xerogel (F) but in this case CPTES was used instead of CETES. The molar ratio of TEOS/CPTES = 4:1. The white product yield was equal to 20.0 g.

Elemental analysis of all the substances prepared was made at the Analytical Laboratory of the Department of Chemistry of UMIST. The potentiometric titration was performed on a multipurpose ionometer EV-14 using 0.05 *N* solution of NaOH in 0.05 *M* solution of KNO_3 [22]. The amount of the sample used was about 0.2 g.

Thermogravimetric curves were recorded on a derivatograph Q-1500 D (MOM, Hungary) in the temperature range from 25 to 1000 ºC (the heating rate was equal to 5ºC/min). Scanning electron micrographs (SEM) were obtained with a JEOL Superprobe 733 microscope.

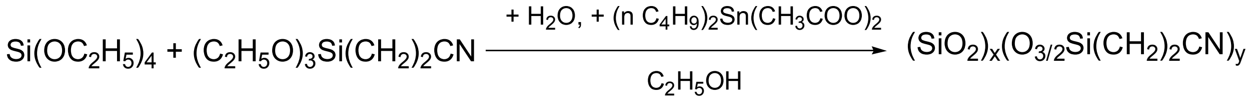
Nitrogen adsorption isotherms were measured at –196ºC by using an ASAP 2405N adsorption analyser (Micromeritics, Inc.) and used to evaluate the BET specific surface area and single-point pore volume [23, 24]. Prior adsorption measurements each sample was degassed at 200ºC. The BET surface area (S) was evaluated in the 0.05 – 0.20 range of relative pressures. This relatively narrow range was used because the samples studied possess pores on the borderline between micro- and mesopores. The single-point pore volume (V) was calculated by converting the amount adsorbed at a relative pressure about 0.99 to the volume of liquid adsorbate. The average pore size was estimated by using the formulae $w_{ar}=4V/S$, valid for cylindrical pores. Pore size w_m at the maximum of the pore size distribution was obtained according to [25].

The IR spectra were recorded on a spectrophotometer Spectrum-1100 (Perkin-Elmer). Prior IR measurements each sample was prepared in the form of suspension in nujol oil (or CCl_4) as well as in the form of pellets with KBr.

All the solid-state NMR measurements were recorded on a Bruker DSX 400 spectrometer. Settings for acquiring the ^{13}C CP/MAS NMR at room temperature were as follows: acquisition time 20–30 ms, relaxation delay was 1.0 s, contact time was 1.00 ms. The number of repetitions was 1200–2000 and the spin rate was 4400. The settings for ^{29}Si DP/MAS NMR at room temperature were as follows: acquisition time 5–10 ms, relaxation delay was 60 seconds, the pulse angle was 90°. The number of repetitions was 300–1000 and the spin rate was 4400. TMS was used as the standard for the NMR experiments.

Results and Discussion

There are several approaches to the synthesis of functionalized silicas containing carboxyl groups. The most popular approach involves the synthesis of materials with nitrile groups followed by their subsequent acid hydrolysis [6–9, 19]. Initially, this type approach was selected for the synthesis of xerogels with carboxylic groups; its first step involves hydrolytic polycondensation reaction (in the presence of catalyst, *n*-$(C_4H_9)_2Sn(CH_3COO)_2$; see scheme *1*) that yields xerogel with nitrile groups (sample A).



$$Si(OC_2H_5)_4 + (C_2H_5O)_3Si(CH_2)_2CN \xrightarrow[C_2H_5OH]{+\ H_2O,\ +\ (n\ C_4H_9)_2Sn(CH_3COO)_2} (SiO_2)_x(O_{3/2}Si(CH_2)_2CN)_y$$

(1)

Indeed, the IR spectrum of the synthesized FPX exhibits absorption bands related to C–H vibrations (2983 – 2934 cm^{-1}), nitrile groups (2262 cm^{-1}), and siloxane bonds (1061 – 1162 cm^{-1}) [26], which confirms the formation of polysiloxane xerogel with nitrile groups. However, the synthesized xerogel turned to be a nonporous solid (surface area < 2.0 m^2/g). Therefore, it is unlikely that any subsequent hydrolysis of this sample would result in adsorbent having a well-developed porous structure. Therefore, another attempt was made to synthesize xerogel with carboxylic groups (sample B). The synthesis procedure was a combination of two processes: namely, hydrolytic polycondensation and saponification of nitrile groups. In this case, an acid catalyst was used instead of a base catalyst that was a mixture of two acids (acetic and sulfuric ones) in water with a component ratio of 1:1:3.

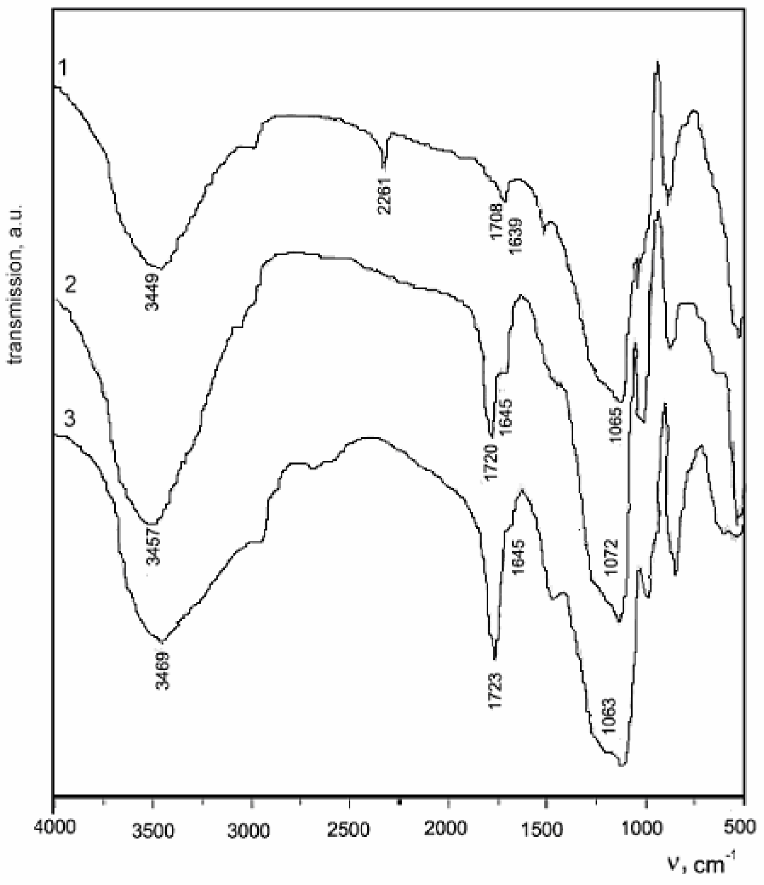


Fig. 1. IR spectra of the synthesized xerogels: **1**- sample B; **2**-sample C; **3**- sample E.

The use of such a mixture for hydrolysis of cyanoalkyl groups attached to the silica surface [9] led to a complete saponification of nitrile groups. In our case, the saponification of nitrile groups was not completed. Thus, the IR spectrum of this sample (Fig. 1, spectrum ***1***) shows absorption bands attributed to vibrations of both nitrile (2261 cm^{-1}) and carboxylic groups (1708 cm^{-1}). Therefore, from our point of view, such a route of the synthesis of xerogels with carboxylic groups is not very effective. There are two processes competing in this case; namely, saponification and hydrolytic polycondensation. Thus, the selection of proper conditions necessary for a complete saponification of nitrile groups remains still problematic.

Our attention was focused on the third approach that had been only briefly described long time ago [20]. In that case the system underwent a transformation of the nitrile-to-imido-ester conversion (see scheme *2*), which was performed by passing a gaseous hydrogen chloride and subsequent introduction of 96 % ethanol. During this process the imido-ester hydrolysis and hydrolytic polycondensation reaction took place and a gel was formed.

The samples prepared in this way do not contain nitrile groups as evidenced by IR analysis (Fig. 1, ***2*** and ***3***). Indeed, in the 2200 – 2300 cm^{-1} range there are no absorption bands related to vibrations of nitrile groups. Elemental analysis of the synthesized substances confirmed that these samples did not contain nitrogen (Table 1).

$$(C_2H_5O)_3Si(CH_2)_2CN \xrightarrow[+\ C_2H_5OH]{+\ HCl_{(g)}} (C_2H_5O)_3Si(CH_2)_2C(OC_2H_5)NH\cdot HCl \xrightarrow[-C_2H_5OH,\ -NH_4Cl]{+\ Si(OC_2H_5)_4,\ +\ H_2O,\ +\ HCl}$$

$$\longrightarrow (SiO_2)_x(O_{3/2}Si(CH_2)_2COOH)_y \qquad (2)$$

The white powder xerogels (samples C, D, E, and F) synthesized by using the latter approach are composite particles of different form (mostly irregular), as it can be seen on the SEM images of the sample C (Fig. 2). Sometimes, beside the above mentioned particles other shapes with layer-type edges can be observed (see Fig. 2, ***b***).

Table 1. Data of elemental analysis, thermal analysis (content in wt %) and potentiometric titration for xerogels with carboxylic groups.

Sample	Elemental Analysis			Thermal Analysis		Concentration of COOH groups, mmol g^{-1}
	C	H	Si	H_2O	Organic part	
C	7.0	3.0	31.4	17.1	14.3	0.97
D	6.2	3.4	30.2	22.9	12.1	0.94
E	11.8	4.4	-	-	-	1.30
F	8.9	3.8	24.5	24.0	15.5	1.10

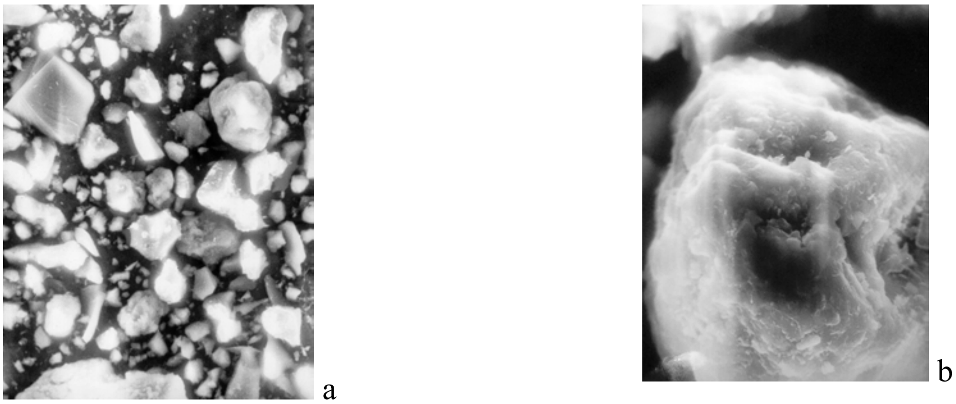


Fig. 2. Scanning electron micrographs of the sample C : ***a***: × 100; ***b***: × 500.

The all samples studied exhibit an endothermal event reflecting the water loss at the temperature interval between 20 and 135^0C. Table 1 shows that different conditions of drying of the samples – under vacuum (C) and under atmosphere pressure (D) – do not greatly influence the content of water. Heating in air above 300°C caused a mass loss that was related to full oxidation of organic groups (see Table 1). The samples C and D were decarboxylated at the temperature of 438°C. Two exothermal events, at 375 and 640^oC, were observed for the sample F.

Table 1 shows the carboxylic group content for each of the xerogels studied. These data were obtained under assumption that the carboxyl-containing alkyl chain has three (samples C, D and E) and four (sample F) carbon atoms, because hydrolytic polycondensation causes a full hydrolysis of triethoxysilyl groups. However, the potentiometric titration results (see Table 1) point out that the content of carboxyl groups is twice smaller than that calculated on the basis of elemental analysis data. To get better understanding let us reanalyse the IR spectra of carboxyl-containing xerogels. Fig. 1 shows that spectra ***2*** and ***3*** are typical for the xerogels functionalized by using a direct method. They contain the most intensive absorption bands in the region of 1050–1150 cm^{-1} that usually has a shoulder. The appearance of this band is typical for the three-dimensional framework of siloxane bonds, ≡Si-O-Si≡ [27]. In the range of 2800–3000 cm^{-1} there was absorption band characteristic of C–H vibrations. According to the data of thermal analysis all the xerogels contain the same amount of water (see Table 1), therefore above 3000 cm^{-1} their IR spectra show intensive and quite wide band of vibrations $\nu(OH)$. Also, one can expect the appearance of less intensive bending $\delta(H_2O)$ at 1630 cm^{-1}. The IR spectra of all carboxyl-containing xerogels are quite similar, except the range of 1600–1725 cm^{-1}. In this range except absorption band at 1720 cm^{-1} (sample C) or 1723 cm^{-1} (sample E), which characterise –COOH group [26], one more absorption band was observed at 1645 cm^{-1} (samples C, E). We can assume that in the case of these xerogels a part of carboxyl groups participates in creation of the ester bond and it is not available for titration. If so, the absorption band at ~1645 cm^{-1} in the IR spectra of xerogels C and E can be referred to the valence vibration of carbonyl group ν(C=O) (Fig. 1, ***c*** and ***d***). Earlier Lisichkin and co-authors also reported analogous situation for silicas with carboxylic groups [22] and assumed the appearance of the ester bonds between the carboxylic and silanol groups $\equiv Si–O–C(O)(CH_2)_2Si\equiv$.

Investigation of ^{13}C CP/MAS NMR spectrum of the sample C (Fig. 3, ***a***) dried in vacuum, confirmed the formation of ester groups during synthesis.

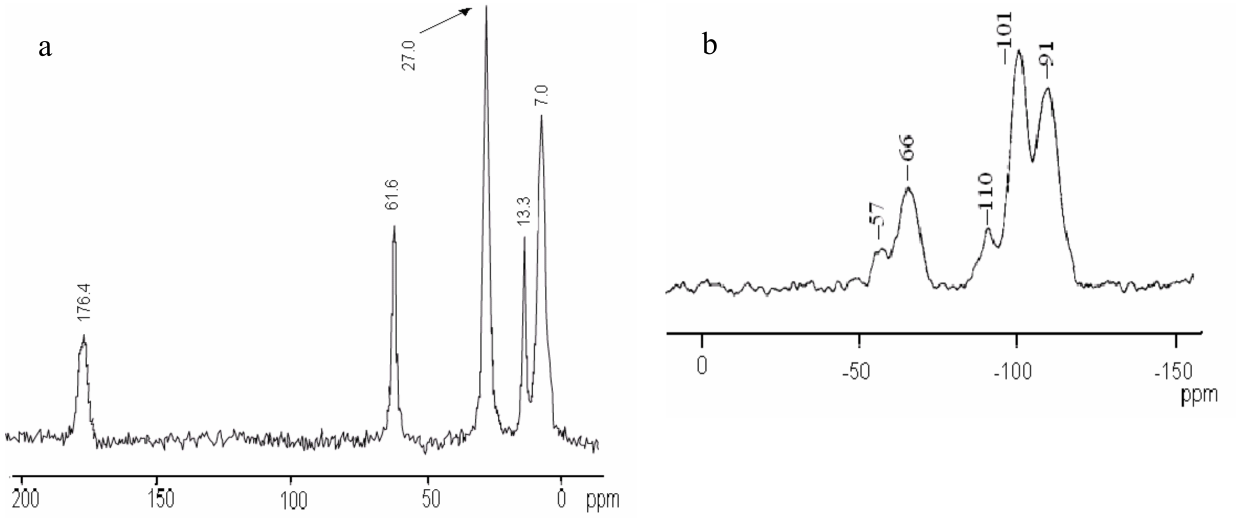


Fig. 3. ^{13}C CP/MAS NMR (***a***) i ^{29}Si DP/MAS (***b***) NMR spectra of xerogel C.

Besides, these data show that the ester groups in the case of the xerogels studied are as follows: $\equiv Si(CH_2)_2C(O)OC_2H_5$. It was proved by the existence of two signals at 13.3 and 61.6 ppm on the spectrum that refer to the carbon atoms in alcohol chain $CH_3–CH_2–O–$. The absence of the signals at ~17 i ~58 ppm on the spectrum, typical for the carbon atoms in ethoxy groups, proved the completion of hydrolysis in the latter. Other three signals can be referred accordingly to the carbon atoms in $\equiv Si–CH_2–CH_2–C(O)O–$ [28]. It should be mentioned that the existence of two groups: $\equiv Si\text{-}CH_2\text{-}CH_2\text{-}COOH$ and $\equiv Si(CH_2)_2C(O)OC_2H_5$, found its reflection in the pattern at 176.4 ppm (Fig. 3, ***a***).

^{29}Si DP/MAS NMR spectrum of xerogel C at –110 to – 50 ppm contains two sets of resonance signals referring to different structure units (Fig. 3, ***b***). The first range contains two intensive and one more weak signals at –110, –101 and –91 ppm, that accordingly refer to the Si atoms in the units of $(SiO)_4\mathbf{Si}$ (Q^4), $(SiO)_3\mathbf{Si}OH$ (Q^3) and $(SiO)_2\mathbf{Si}(OH)_2$ (Q^2) [29]. The second range has one signal at –66 ppm with intensive shoulder at –57 ppm appropriate for the structure units of $(SiO)_3\mathbf{Si}R'$ and $(SiO)_2\mathbf{Si}(OH)R'$, where R' – carboxyl-containing chain. The existence of such set of structure units is a typical picture of FPX, indifferently from the nature of the functional groups and the structure-adsorption characteristics [30].

Table 2 lists the structure-adsorption characteristics of the samples studied. As can be seen from this Table, the synthesized xerogels have well-developed porous structures. Their specific surface areas are high (370 – 680 m^2/g). The average pore diameter determined under assumption of cylindrical pores was on the borderline between micro- and mesopores. An increase in the surface area was observed when the ratio changed from 2:1 (Table 2, sample E) to 4:1 (sample C or D). The surface areas increases even more when propyl chains (sample F) are changed into ethyl groups (sample C).

Table 2. Adsorption characteristics of xerogel samples

Sample	S_{sp}, m^2g^{-1}	V_s, cm^3g^{-1}	w_{ar} (w_m) nm
C	675	0.37	2.2 (1.7)
D	680	0.36	2.1 (1.8)
E	370	0.23	2.5 (1.7)
F	520	0.26	1.9 (1.5)

Comparing the texture characteristics of xerogels synthesized under acidic conditions (Table 2) with the same characteristics for the xerogels obtained in the alkaline medium or in non-aqueous solvents with catalysts present such as F^- [15], one can conclude that in all cases the dependence between the synthesis conditions and the texture characteristics is similar.

Conclusions

A simple procedure for the synthesis of functionalized polysiloxane xerogels has been developed. The procedure was based on the sol-gel method involving conversion (under mild conditions) of alkylnitriles of trialkoxysilanes to esters, allowing the synthesis of novel xerogels with alkylcarboxylic groups. The IR and ^{13}C CP/MAS NMR spectroscopy studies showed that some carboxylic groups convert to ester groups, $\equiv Si(CH_2)_{2\text{ or }3}C(O)OC_2H_5$. Nitrogen adsorption studies showed that these materials were possessed the well-developed micro-mesoporous structures evidenced by high surface areas (S_{sp} = 370 – 680 m^2/g) and the size of pores on the borderline between micropores and mesopores (w_{ar} = 1.9 – 2.5 nm). These materials seem to be promising for application to adsorption technology, chromatography, and other related areas.

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ИСПОЛЬЗОВАНИЕ ЗОЛЬ-ГЕЛЬ МЕТОДА ДЛЯ ПОЛУЧЕНИЯ ПОЛИСИЛОКСАНОВЫХ КСЕРОГЕЛЕЙ, ФУНКЦИОНАЛИЗОВАННЫХ КАРБОКСИЛЬНЫМИ ГРУППАМИ

О.А. Дударко[1], Ю.Л. Зуб[1], М. Яронец[2], М.Дж. Вайт [3], Квихуа Янг[4]

[1]Институт химии поверхности им. О.О. Чуйко Национальной академии наук Украины,
17, ул. Генерала Наумова, г. Киев 03164 Украина
[2]Отдел химии, Университет г. Кент, Огайо, 44242, США А
[3]Школа химической технологии Дэйва Си. Сволма, Государственный университет
Миссисипи,330 Сволм Билдинг химической технологии, Миссисипи, 39762, США
[4] Даляньський Институт химической физики, ул. Зондсхан 457, Далянь, 116023 Китай

Разработана методика синтеза новых полисилоксановых ксерогелей, содержащих остатки пропионовой и масляной кислот. Методами ИК и ^{13}C *CP/MAS ЯМР спектроскопии установлено, что часть карбоксильных групп существует в полученных ксерогелях в виде эфирных групп,* $\equiv Si(CH_2)_{2\text{ или }3}C(O)OC_2H_5$*. Анализ изотерм адсорбции азота показал, что синтезированные образцы обладают высокой удельной поверхностью (370−680 м*^{2}*/г), а средний диаметр их пор находится на границе микро-мезопористости и составляет 2,1 – 2,2 нм.*

ВИКОРИСТАННЯ ЗОЛЬ-ГЕЛЬ МЕТОДУ ДЛЯ ОДЕРЖАННЯ ПОЛІСИЛОКСАНОВИХ КСЕРОГЕЛІВ, ФУНКЦІОНАЛІЗОВАНИХ КАРБОКСИЛЬНИМИ ГРУПАМИ

О.А. Дударко[1], Ю.Л. Зуб[1], М. Яронець[2], М.Дж. Вайт[3], Квіхуа Янг[4]

[1]Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України, 17, вул. Генерала
Наумова, м. Київ 03164 Україна
[2]Відділ хімії, Університет м. Кент, Огайо, 44242, США
[3]Школа хімічної технології Дейва Сі. Сволма , Державний університет Міссісіпі, 330 Сволм
Билдінг хімічної технології, штат Місісіпі, 39762, США
[4]Даляньський Інститут хімічної фізики , вул. Зондсхан 457, Далянь, 116023 Китай

Розроблена методика синтезу нових полісилоксанових ксерогелів, що містять залишки пропіонової і масляної кислот. Методами ІЧ та ^{13}C *CP/MAS ЯМР спектроскопії встановлено, що частина карбоксильних груп в одержаних ксерогелях існує у вигляді ефірних груп* $\equiv Si(CH_2)_{2\text{ або }3}C(O)OC_2H_5$*. Аналіз ізотерм адсорбції азоту показав, що синтезовані зразки мають високу питому поверхню (370–680 м*^{2}*/г), а середній діаметр їх пор перебуває на межі мікро-мезопористості і складає 2,1–2,2 нм.*