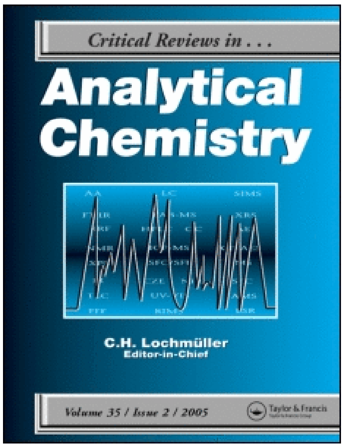

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Characteristics, Chemical Modification Processes as well as the Application of Silica and its Modified Forms

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The variety of chemical modifications of the surface of silica and its modified forms cause these materials to find a consistently wider scope of application. In the publication, the characteristics of silica, silica gel, aerogel and xerogel are presented. The obtainment, application and properties of these materials are discussed. Methods of chemical modifications of surface structures with the use of different chemical compounds are presented. Special attention is turned to the behavior of silica and its modified form during the adsorption process. The main applications of silica and its different forms in analytical chemistry are also discussed.

Keywords Chemical modification, silica, silica gel, xerogel, aerogel

INTRODUCTION

During technological processes and while conducting analyses, materials are used which should contain a defined surface structure. The usefulness of these materials for concrete applications is the result of chemical and physical effects of chemical substances present on their surfaces. General examples of these materials are: wood coal, cosmetic talc, calcium carbonate, graphitized soot, diamonds, cellulose, clay compounds, silica gel, molecular screens (claysilicate of alkali metals), carbonaceous molecular screens, porous polymers as well as other solid bodies (1). The limited usefulness of many materials, resulting from inadequate surface properties, is the subject of many studies being conducted in scientific laboratories.

For many years, a search for new methods of chemical surface modifications has been conducted for different forms of silica (2–5). The presence of hydroxyl on the surface of silica materials greatly facilitates their modification, which allows for their wide application in analytical chemistry.

CHARACTERISTICS OF SILICA AND ITS MODIFIED FORMS

Silica is a basic component of a few generally used materials. These are: silica gel, aerogel and xerogel.

Silica

Silica is the final product of a very slow silicon arrangement under the influence of water and carbon dioxide. It appears in nature in large quantities, as sand. It usually contains different pollutants. Marine sand is almost clean silica. Depending on the form in which it appears and dyes silicon oxide, it creates different minerals.

Silica is a solid and very hard substance. Silicon dioxide melts at a temperature of 1723°C (it can be lowered with the addition of so-called fluxes). The boiling temperature is even higher, at 2230°C. Silica is very chemically resistant and reacts solely with boiling, concentrated water solutions, KOH and NaOH, melted Na_2CO_3 and K_2CO_3, gaseous hydrofluoride (HF) as well as a contentrated solution of this gas in water, called carbonatefluoride acid. In results of silica's reaction with KOH, NaOH, Na_2CO_3 and K_2CO_3, certain salts appear—salt and potassium silicate—which are soluble in water and sold as so-called water glass (6).

This compound can be classified on the basis of four basic characteristics:

- crystalline structures
- dispersion
- surface composition
- porosity

Silica is the most disseminated adsorbent, being a chemical carrier for connected stationary phases. Many surface modification methods exist for this adsorbent. Two methods dominate in the literature. One depends on the hydrolyzation of the

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silicon atoms located in siloxane connections (≡Si—O—Si≡). The second, more traditional, method consists of different types of organosilanes containing active chloro-, methoxy-, ethoxy- or amino- groups, which are chemically connected with the surface of the carrier.

A general, the summary silica formula (SiO_2) does not do a good job of representing its factual chemical structure (Figure 1). In reality, it creates an expanded special structure in which almost every silicon atom is connected to four oxygen atoms, whereas almost every oxygen atom connects itself with two silica atoms. However, many defects appear in this network. Additionally, the surface of the silica can contain many hydrogen, alkaline metals or hydroxyl group atoms, depending on their origins (6).

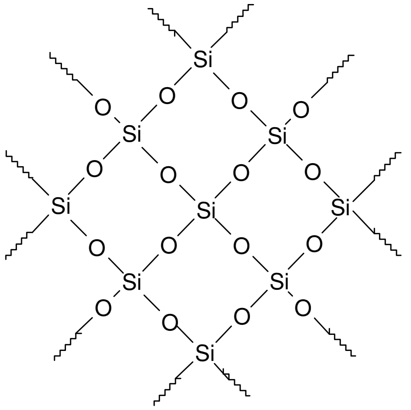
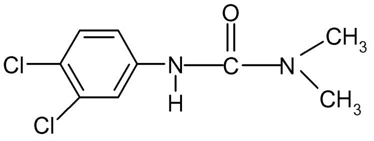
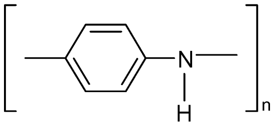
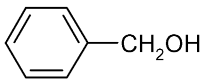
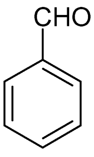
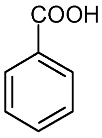
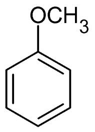
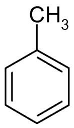
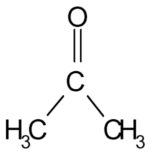
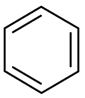
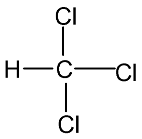
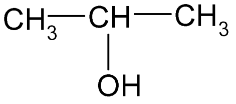


FIG. 1. Idealized diagram of a realistic silica structure **(6)**.

TABLE 1
Characteristics of three forms of silica **(12, 13)**

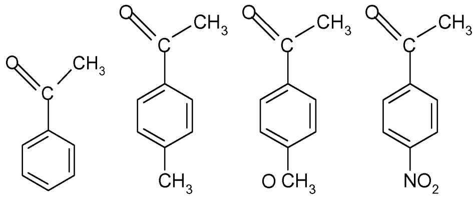
	Silica gel	Xerogel	Aerogel
Obtainment	- Created by hydrated silica particles (dioxide silicon)	- The body was created from gel by drying and shrinking	- First, in results from melting ideally clean silica in the atmosphere, overcritical carbon dioxide and "blowing out" with the help from organic solvent steam by a gradual decrease in pressure - From the results of the chemical method consisting of a reaction of extremely thin four-function alcylxysilane with water steam ($Si(OCH_3)_4$) in any atmospheric gas
Properties	- Shape, as well as porous structure, remains unchanged, even after complete drying - Possesses very efficient drying properties - Useful physiochemical properties (14, 15) - Mechanical durability (does not get destroyed under pressure up to 65 MPa) - Chemical volume (pH range 2-8) - Durable in temperatures up to 250°C - Possibility of substituting silicon atoms in the gel with other atoms (e.g., boron, magnesium or aluminum).	- High porosity (25%) along with a very small pore size (1–10 nm)	- A type of stiff foam with exceptionally low density - 90–99.8% air, the rest is a porous material which creates its structure - Currently the lightest solid substance - Density of 1.9–150 mg/cm^3, not much higher density than air (1.2 mg/cm^3) - Smallest material for solid bodies which are co-factors in heat leadership (16) - Durable up to silica's melting point (around 1200°C)
Application	- Means of drying the gases in an exsiccator - Filler in rubber products - Catalyst carrier, etc.		- Material used for building spaceships - Isolating layer in cosmonaut's suits - Thermo-isolating filler in airplanes - Used as a base for catalysts for some chemical reactions because of its highly developed surface (11).

TABLE 2
Basic information about chemical processes modifying the surfaces of silica and silica gel

Type of modified surface	Compounds used for chemical modification	Effects of the modifications
Silica gel	(3-(3,4-dichlorophenyl)-1,1-dimethylurea) 	- Immobilization of the pesticides on the surface of the silica gel (22)
Silica gel	polyaniline 	- Ability to stop metal pollution of the environment (23, 24)
Silica gel	benzyl alcohol  benzaldehyde  benzoic acid  anisole  toluene 	- Possibility of attaching an aromatic adsorbent to the silica gel surface (25, 26)
Silica gel	acetone  benzene  chloroform 	- Adsorption at a high acetone, benzene and chloroform temperature on the surface of the silica gel (27)
Silica	1-propyl alcohol $CH_3-CH_2-CH_2-OH$ isopropyl alcohol  $CH_3-CH(OH)-CH_3$	- The adsorption of 1-propyl alcohol and isopropyl alcohol was studied, on the surface of a cyclohexane mixture with the use of FTIR spectroscopy in ATR format (28). Isothermic adsorption showed adsorption similar to the amount of each alcohol, while FTIR spectroscopy showed the presence of hydrogen connectors between the surface of the silane groups and –OH 1-propanol groups. A similar surface modification has been proposed by scientists (29), who modify silica through ethanol adsorption on its surface.

(Continued on next page)

TABLE 2
Basic information about chemical processes modifying the surfaces of silica and silica gel (*Continued)*

Type of modified surface	Compounds used for chemical modification	Effects of the modifications
Silica	four types of acetophenones 	It has been concluded that a hydrogen connector between the silane and carbon groups is responsible for adsorption. It has been proven that adsorption by substituting benzene depends on the electron influence of the substitute. However, during dioxin adsorption on non-porous and micro-porous silica is the result of the volume and size of the measurements (30, 31). The obtained silica was analyzed using the IR technique.
Porous silica	(N,N-dimethylamino)-alkyldimethylsilane 10-bis(trimethylsiloxymethylsilyl)-decyldimethylchlorosilane	Four modified silica forms were obtained (32–38): octyl-silica, hexadecyl-silica, bis(trimethylsiloxy)-silica and oligo(dimethylsiloxane)-silica. Their adsorption properties were measured.
Silica	butane and butene	Butane and butene adsorption (39) was analyzed on a silica surface in different temperatures, and physical and chemical changes in the silica were described. A highly hydrated silica was the result of butane and butene adsorption, which was measured with the use of IR spectroscopy (40). This experience confirms that the complex nature of the silica surface is mainly the result of its micro-porosity and the presence of a hydroxyl group on its surface (41, 42).

Silica Gel, Xerogel, Aerogel

Amongst the main forms of silica showing good dispersion, the following can be distinguished: silica gel, xerogel and aerogel (7–11). The basic characteristics of these materials are presented in Table 1.

Silane groups (Si-OH), which are common for the above-mentioned materials, represent reactive places, allowing for structural surface modification. Depending on the initial treatment of the surface structure, the following silane group types were distinguished (7–11): silanediol, silanetriol, neighboring hydroxyl groups and hydroxyl groups connected with hydrogen connectors (Figure 2).

CHEMICAL MODIFICATION PROCESSES FOR SILICA SURFACES AND SILICA GEL USING DIFFERENT CHEMICAL COMPOUNDS

For many years, a search has been ongoing for new chemical modification methods derivative of different forms of silica (Table 2). In the studies, many different analytical methods were applied with the aim of changing the surface properties of these sorbents, the topography, inner-surface energy, pore size, etc. It was discovered that an important role in the application of these materials is played by the adsorption characteristics and the structure of the modified silica (14, 17–21).

OBTAINING HYDROPHOBIC SILICA AEROGEL

Silica aerogels obtained with the use of tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) are very hydrophilic.

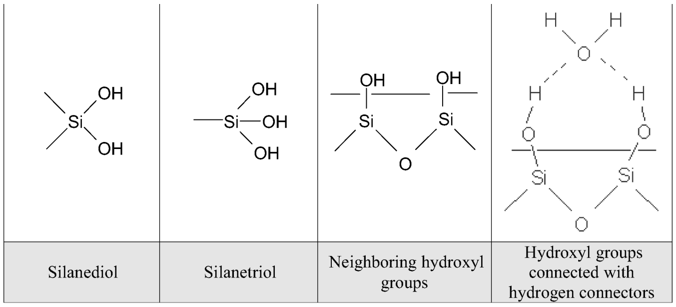


FIG. 2. Silane group types appearing on the surface of different forms of silica (8–12).

Because of this, a slow adsorption process occurs for water particles from atmospheric air. This is caused by the fact that aerogels possess a polar OH group on their surface, which take part in the hydro-information of its contact with H_2O molecules. In results from surface modifications, aerogels can become hydrophobic (17). Such a modification can be carried out, for example, by connecting alkyl or aryl groups, appearing in organosilic compounds: dimethylchlorosilane (DMCS), dimethyldichlorosilane (DMDC), trimethylbromosilane (TMBS), trimethylchlorosilane (TMCS) and trimethylsilylchloroacetate (TMSCA), trimethylmethoxysilane (TMMS). The above-mentioned compounds were used to obtain hydrophobic silica gels.

In Figure 3, photographs of water droplets are presented on modified silica aerogel surfaces. Experiments consist of using a couple hydrophobic reagents consisting of up to three functional groups (18). Their result is the obtainment of hydrophobicity as well as an improvement in the durability of the aerogel. The obtained aerogels were characterized with the use of scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential thermal analysis (DTA), the degree of contact was measured, as well as water adsorption, trimethylmethoxysilane (TMES), tetramethylsilane (TMS) and hexamethyldisilane (HMDS).

Information from results of analysis of the obtained aerogel samples is presented in Table 3 (physical properties) and Table 4 (hydrophobic properties and thermal stability) (17).

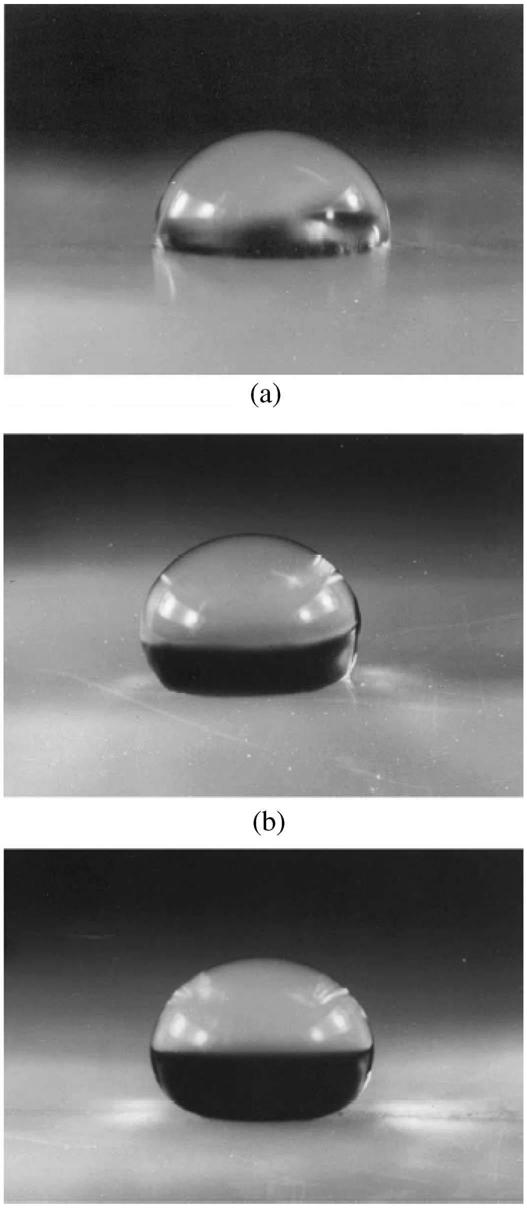
Aerogels obtained during modification processes with the help of HMDS (Table 3) underwent a gelling process almost immediately, and the pH was maintained around 9. This was because of the presence of amino groups contained in HMDS, which in turn, influenced the quickening of the condensation pace, causing the gelling to occur faster. It was proven that organosilanes containing chlorine (e.g., DMDS, TMCS) reacted with OH groups on the surface of the silica aerogel with the

TABLE 3
Physical properties of silica aerogel obtained from the application of different organosilic mixtures (21)

Hydrophobic component	Gelling time T_g (h)	Bulk density, ρ(g/cm^3)	Porosity, P (%)	Transparency, T (%)	Volume, shrinkage V_s (%)	Comments
MTMS	2.5	0.1315	93.73	88	12.39	Monolithic
DMCS	3.7	0.1833	91.27	10	28.90	Connected
DMDC	12	0.1955	90.69	8	32.77	Connected
TMCS	72	—	—	5	—	Powder
TMSCA	5 months	—	—	5	—	Powder
TMBS	70	0.2346	88.82	7	47.96	Individual cracks
TMMS	1.6	0.1391	93.37	80	23.72	Monolithic
TMES	2.1	0.09696	95.38	90	20.19	Monolithic
TMS	2.1	0.09674	95.39	91	15.18	Monolithic
HMDS	0.1	0.1253	94.03	70	28.29	Multiple cracks

TABLE 4
Hydrophobic and thermal properties of silica aerogel obtained with the use of different organosilic compounds (21)

Hydrophobic component	Short form	Contact angle β (°) Photography method	Contact angle β (°) Counting method	Growth in the aerogel mass after being held inin in water for 3 months	Thermal durability (°C)
Methyltrimethoxysilane	MTMS	95	94	7%	277
Dimethylchlorosilane	DMCS	98	100	13%	275
Dimethyldichlorosilane	DMDC	120	119	7%	298
Trimethylochlorosilane	TMCS	—	—	Hydrophobic powder	290
Trimethylsilylchloroacetate	TMSCA	—	—	Hydrophobic powder	300
Trimethylbromosilane	TMBS	—	—	9%	300
Trimethylmethoxysiane	TMMS	125	123	9%	295
Trimetyletoxysilane	TMES	102	100	12%	300
Tetramethylsilane	TMS	0	0	>100%	<100
Hexamethyldisilane	HMDS	135	133	5%	300



(a)

(b)

(c)

FIG. 3. Water droplets on modified silica aerogel surface with the use of different compounds: (a) MTMS ($\beta = 95°$); (b) TMMS ($\beta = 125°$); (c) HMDS ($\beta = 135°$) (21).

secretion of HCl, resulting from the chemical reaction (16, 21, 22):

$$\equiv \mathrm{Si{-}OH} + \mathrm{Cl_xSi(R)_{4-x}} \rightarrow \equiv \mathrm{Si{-}O{-}Si(R)_{3-x}Cl_{x-1}} + \mathrm{HCL} \qquad [1]$$

$$\mathrm{(R)_{4-x}SiCl_x} + \mathrm{H_2O} \rightarrow \mathrm{(R)_{4-x}SiCl_{x-1}OH} + \mathrm{HCL} \qquad [2]$$

where x = 1,2 or 3 and R is the alkyl group.

The presence of HCl in the colloidal solution containing HMDS gelled in a couple of minutes (Table 4) (20). Aerogels prepared using MTMS and TMS were characterized by lower volume ($V_S < 15\%$) in comparison with aerogels containing TMBS ($V_S = 48\%$) and DMDC ($V_S = 32\%$). Differences in gained volume of aerogels influenced their thickness. Aerogels obtained using TMS and MTMS were characterized by lower thickness, around 0.1 g/cm^3 and higher porosity, around 95%; however, aerogels prepared with the use of TMBS contained a thickness of 0.23 g/cm^3 and porosity of about 88%. It was also determined that silica aerogels prepared with use of organosiles containing metalohalogenic were turbid (clearness < 8%), and aerogels prepared with alkylalcoxysilanes were clear (80%).

PREPARING STANDARD GAS MIXTURES

A big challenge for both manufacturers and users is posed by, also called standard gas mixtures. In the case of preparing standard gas mixtures of toxic, reactive and badly smelling substances, the production of the exactly defined amounts of analytes via thermal decomposition of surface compounds is the original methodological approach.

This approach is based on using surface compounds that are chemically bound to the carrier's surface (e.g., silica gel, porous glass, glass rods covered with silica gel and glass fibers) and undergo thermal decomposition or chemical regrouping that results in a release of the precisely specified amount of a volatile compound. The released compounds are washed out from the reaction chamber (e.g., chromatographic injector or thermal desorber) with a stream of diluting gas which now becomes a stream of standard gas mixture.

TABLE 5
Possible ways of producing volatile analytes via thermal decomposition of appropriate surface compounds (43–59)

Carrier type	Released volatile analyte	Literature
Silica gel	CO, CO_2	(43, 44)
	CO_2	(45)
	C_2H_4	(46)
	CH_3Cl	(47, 48)
	NH_3	(49)
	CH_3NH_2	(49)
	$(C_2H_5)_2NH$	(49)
	$(C_2H_5)_3N$	(49)
	CH_2CHCH_2NCS	(50)
	C_4H_9NCS	(50)
	CH_3SH	(51)
	C_3H_7SH	(52–54)
	CH_3CHO	(55)
Rods covered with silica gel	CO, CO_2	(56)
Porous glass	C_2H_4	(57)
Glass fibers	C_2H_4	(58)
Fiberglass	CH_3Cl	(59)

TABLE 6
The main range of applications for silica and silica gel in analytical chemistry

Compound	Application	Literature
Silica	One of the basic materials for capillary column manufacturing in gas chromatography: - the column is covered with polyimide with the aim of extension of its exposure to high temperatures (upper limit temperature of the column is 360°C); - the inner surface of the column is chemically deactivated to lower the effects between the sample and the column. The applied process and the reagents depend on the stationary phase type covering the column. For most of the columns, a silylation process is applied. Silane groups (Si–OH) on the surface of the column react with silane reagents. Usually, for the majority of columns, surfaces with metal groups or phenylmethylosilane surface types are created.	(60, 61)
	Stationary phases with different liquid chromatography variations surpass their application in reverse phase (RP) HPLC: - a phase modified by hydrophobic hydrogen chains with different lengths (C_2, C_8, C_{18}, C_{22}, C_{30}) find application in pharmacological determination, as well as clinical and biochemical, and for environmental and foodstuff analysis. - Its synthesis is highly repeatable, and chromatographic processes related to mass transport, are highly useable.	(60)
	The stationary column phase for HPLC: - currently, over 400 okatadecyl stationary phases are available based on silicon oxide, not counting polar phases of modified surfaces; - silicon oxide has a more homogenic surface (from an HPLC perspective) than other oxide metals (TiO_2, Al_2O_3, ZrO_2) and it can also tolerate pressure above 70 MPa.	(61-63)
	In solid phase extraction (SPE), universal silica, with a high value of organic carbon related to the surface, is used; modified silica.	(64, 65)
Silica gel	Adsorbent used for filling the column in adsorbent gas chromatography: - with the aim of separating gas mixtures containing carbon dioxide as well as when analyzing light hydrocarbons; - phosgene analysis, as well as hydrochloric, chlorine, and gaseous sulphur compounds, e.g., sulphuroxide carbon, sulphurcarbon, disulphur carbon and sulphur dioxide.	(66–68)
	Polyaniline covered in silica gel used for stopping metal pollution in the environment using adsorption (among others, in liquid sewage, polluted with groundwater.	(24)
	In thin layer chromatography (TLC): - as a separating phase, deposit, or in other words, the stationary phase with sorption properties. It is placed as a thin layer (up to 1–2 mm) on a glass, metal, or artificial-material plate; - for separating all classes of compounds, depending on gel preparations.	(69)
	Immobilize artificial membrane (IAM) stationary phase, in which phospholipid molecules were conventionally connected to the silica surface carrier: - with the aim of effective low-molecule protein separation (albumin).	(70)
	Surface compound carrier (ethene, methyl chloride).	(71–74)
	In liquid chromatography and related techniques, stationary phases with polar functional groups, such as $-NH_2$, $-NO_2$, -CN, etc. (Figure 4).	(71–74)
	In solid phase extraction (SPE): - as a filler for extraction of any or acidic alcylophenyl compounds. With this aim, silica gel is modified with oktadecyl groups C_{18} (extraction productivity above 80%).	(79, 80)
	- Filling for gel permeation chromatography (GPC).	(81)

The present extent of the above-mentioned approach's application for preparation of standard gas mixtures, which constitute a specific type of matrix-free reference materials, are presented in Table 5 (43–59).

THE APPLICATION OF SILICA AND SILICA GEL IN ANALYTICAL CHEMISTRY

Silica and silica gel has found a wide scope of application in analytical chemistry. Information on the basic range of application for silica and its different forms in analytical chemistry is presented in Table 6.

SUMMARY

Silica is a material which currently has a very highly analyzed surface. The presence of active hydroxyl groups on the surface of this material facilitates its modification. Because of this, silica and its different forms become promising materials for numerous types of chemical reactions on its surface. In the future, modified silica can be applied in industry, biology and in pharmacology (82–86) .

ACKNOWLEDGMENTS

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LIST OF ACRONYMS AND ABBREVIATIONS

Acronym/abbrev	English term
DMCS	Dimethylchlorosilane
DMDC	Dimethyldichlorosilane
DTA	Differential thermal analysis
GC	Gas chromatography
HMDS	Hexamethyldisilane
HPLC	High performance liquid chromatography
MTMS	Methyltrimethoxysilane
OSC	Organosilicon compounds
P	Porosity
ρ	Bulk density
SEM	Scanning electron microscopy
SiO_2	Silica
T	Transparency
TEOS	Tetraethoxysilane
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
TMBS	Trimethylbromosilane
TMCS	Trimethylchlorosilane
TMES	Trimethylethoxysilane
TMMS	Trimethylmethoxysilane
TMOS	Tetramethoxysilane
TMS	Tetramethylsilane
TMSCA	Trimethylsilylchloroacetylene
T_g	Gelation time
V_s	Volume shrinkage
β	Contact angle

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