UNIVERSIDAD NACIONAL DE COLOMBIA

Development of silica containing materials for the adsorption of organic compounds

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Manizales, Colombia
2011

Desarrollo de materiales a base de sílice para la adsorción de compuestos orgánicos

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Thesis submitted as partial requirement to obtain the title of:
Master of Engineering - Chemical Engineering

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Line of enquiry:
Process intensification and hybrid systems
Research group:
Grupo de Investigación en Aplicación de Nuevas Tecnologías (GIANT)

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2011

To my parents
Noé Duque and Stella Salazar

And to my siblings
Laura Inés Duque and Marcin Jędrzejczyk

“Challenges are what make life interesting;
overcoming them is what makes life
meaningful."

Joshua J. Marine

Acknowledgements

I wish to express my deepest gratitude to my supervisor Izabela Dobrosz-Gómez for your guidance, supervision, support and friendship. Gratitude is also expressed to my Professors Javier Fontalvo and Miguel Ángel Gómez for their teachings, help and support. Very special thanks go to Professor Jacek Rynkowski who allowed me have an important experience in my life during my internship in the Institute of General and Ecological Chemistry of Technical University of Lodz, Poland.

I would like to thank to Universidad Nacional de Colombia, Dirección de Investigaciones Sede Manizales (DIMA) and COLCIENCIAS for the financial support of this research through the projects "Implementación de métodos químicos de preparación de materiales nanoparticulados para aplicaciones tecnológicas" and "Jóvenes Investigadores e Innovadores - Virginia Gutiérrez de Pineda 2009", program financed by COLCIENCIAS and Universidad Nacional de Colombia, Sede Manizales (inter-administrative agreement No 704 of 2009).

My thankfulness goes also to Marcin Jędrzejczyk, my coworker, friend and older brother who was my great support to overcome all challenges in Poland. Thank you for your guidance, support, friendship and interesting discussions about life and science while we shared a cup of Colombian coffee, which made me feel like at home.

Also I thank for the support received by Ph.D. Joanna Bojarska in the XRD measurements, Mr. Piotr Malinowski for SEM microphotographs, Mr. Witold Sowiński for thermal analysis, and Ph.D. Wiola Raróg-Pilecka for BET measurements performed in Poland. Special thank to Beatriz Gálvez for FTIR studies in Universidad Nacional de Colombia, Sede Manizales.

To my colleagues Diana Maria Aguilar, Miguel Duque, Oscar Johnny Jaramillo and Mario Noriega and all the members of research group GIANT, thank you for your company, support and friendship. To my Friends in Colombia Luis Gabriel Loaiza, Edwin Vásquez, Julián Duque, Paula Fernanda García, thanks for encourage me to follow this dream.

To my friends in Poland Paulina Kwintal-Ogórek, Agnieszka Ura Michalak, Agnieszka Ruppert, Elżbieta Maćkiewicz, Karolina Chałupka, Klaudia Nalepa, Aleksandra Królak, Aleksandra Pawlaczyk and Gesualdo Donnarumma, thanks for being my family in Poland, for support and for allowing me to share with you a small part of my beautiful country Colombia.

Finally, I would like to thank to my family, the motor of this dream. Thanks for your continuous encouragement, your support during my entire life and for being my best friends, confidents and allied.

Thanks to everyone!

Summary

Silica gels are ceramic materials with exceptional properties such as high surface area, small pore size and low thermal conductivity. These properties allow applying silica gels as material for catalytic support, thermal and acoustic insulator, adsorbent and membranes. However, the hydrophilic nature of silica causes the adsorption of moisture from the humid surroundings, limiting its practical application. Chemical modification of silica xerogel with hydrophobic agents can prevent the adsorption of water and result in hydrophobic material. This research is focused on the study of hydrophilic and hydrophobic silica xerogels: their synthesis, characterizations and potential applications. A more detailed insight into the different factors controlling the adsorptive properties of silica-derived xerogels is gained. The influence of the physico-chemical properties on their performance as adsorbents of organic compounds (alcohols) and as materials for preparation of inorganic membranes for ethanol removal and purification has been studied. First of all, the study of hydrophilic silica xerogel synthesized by sol-gel method using the standard molar ratio is presented. The influence of aging time and calcination process on hydrophilic silica gel properties is analyzed. Subsequently, the synthesis of hydrophobic silica xerogel by co-precursor and derivatization methods using methyltrimethoxysilane (MTMS) and methyltriethoxysilane (MTES) hydrophobic agents are exposed. The effect of type of hydrophobic agent, preparation method and calcination temperature on the physico-chemical, superficial, morphological textural and adsorptive properties on hydrophobic silica xerogel are discussed. Finally, the potential applications of hydrophilic and hydrophobic silica xerogels as alcohols adsorbent material and membranes are also presented. Therefore, adsorption of methanol, ethanol, butanol, and pentanol on silica materials was performed. The following order of increasing alcohols adsorption capacity was observed: methanol < ethanol < butanol < pentanol. The sequence of increasing adsorption capacity was followed by the sequence of increasing surface tension and molecular weight of the adsorbate. Silica membranes were successfully tested in pervaporation process for ethanol removal (hydrophobic membranes) and ethanol purification (hydrophilic membranes).

Keywords: Silica xerogel, sol-gel method, surface modification, alcohol adsorption, inorganic membranes.

Resumen

Los xerogeles de sílice son materiales cerámicos con propiedades excepcionales tales como alta área superficial, poros pequeños y baja conductividad térmica; las cuales permiten su aplicación como soportes catalíticos, aislantes térmicos y acústicos, materiales adsorbentes y membranas. Sin embargo, la naturaleza hidrofílica de la sílice genera la adsorción de agua en ambientes húmedos, lo cual limita su aplicación. La modificación química de los xerogeles de sílice mediante agentes hidrofóbicos previene la adsorción de agua, generando materiales hidrofóbicos. Ésta investigación se enfocó en el estudio de xerogeles hidrofílicos e hidrofóbicos de sílice: su síntesis, caracterización y potenciales aplicaciones. Se ganó una visión más detallada de los diferentes factores controlantes de las propiedades adsorptivas de los xerogeles derivados de la sílice. Se estudió la influencia de las propiedades físico-químicas en el desempeño como material adsorbente de compuestos orgánicos (alcoholes) y como material para la preparación de membranas inorgánicas para la remoción y purificación de etanol. Inicialmente se presenta el estudio de xerogeles hidrofílicos de sílice, sintetizados mediante el método sol-gel empleando la relación molar estándar. Se analiza la influencia del tiempo de envejecimiento y el proceso de calcinación en las propiedades del material hidrofílico obtenido. Posteriormente se presenta la síntesis de los xerogeles hidrofóbicos de sílice mediante los métodos co-precursor y derivativo usando metiltrimetoxisilano (MTMS) y metiltrietoxisilano (MTES) como agentes hidrofóbicos. Se analiza el efecto del tipo del agente hidrofóbico, el método de preparación y la temperatura de calcinación sobre las propiedades físico-químicas, superficiales, morfológicas, texturales y adsorptivas del material. Por último se presentan las posibles aplicaciones de los xerogeles de sílice como materiales adsorbentes de alcoholes y membranas. Por tanto, se llevó a cabo los estudios de adsorción de metanol, etanol, butanol y pentanol sobre los materiales de sílice sintetizados. La capacidad de adsorción de los alcoholes se encontró en el siguiente orden: metanol < etanol < butanol < pentanol. La secuencia en el incremento de la capacidad de adsorción fue seguida por la secuencia en el aumento de la tensión superficial y el peso molecular del adsorbato. Además, las membranas de sílice se probaron exitosamente en procesos de pervaporación en la remoción de etanol (membranas hidrofóbicas) y purificación de etanol (membranas hidrofílicas).

Palabras claves: Xerogeles de sílice, método sol-gel, modificación superficial, adsorción de alcoholes, membranas inorgánicas.

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Symbol	Definition
[D]	Dimers concentaration
[Ol]	Oligomers concentaration
[R]	Alkoxide concentration
[Tr]	Trimerss concentaration
A	Arrhenious constant
a_{BET}	Specific surface area
C	Constant related with the adsorption energy of the adsorbed monolayer
D	Dimers
E	Activation energy
H	Microporous width
i	Intercept equation (24)
J_i	Mass flux of component i
J_{total}	Total mass flux
k	Reaction rate constant
K	Viscometer constant ($2.10085x10^{-3}$ $cm^2.s^{-2}$),
L	Avogrado constant
M	Monomers
m_0	Amount of initial water-ethanol liquid mixture
m_c:	Amount of dried silica xerogels
m_l	Amount of water-ethanol liquid mixture after adsorption process
n	Amount of gas adsorbed at working pressure
n_m	Amount of the adsorbed gas when the surface is covered with a monolayer
Ol	Oligomers
p	working pressure
p^o	vapor pressure of a gas at adsorption temperature
PSI	Pervaporation separation index
R	Alky-group ($-C_xH_{2x+1}$)
R	Unhydrolyzed species
RW	Amount of liquid mixture adsorbed per gram of dried silica xerogel
s	Slope equation (24)
t	Time at which a ball moves from one place to another
t_g	Gelation time
Tr	Trimers
w_{ip}	Mass fraction of preferential component in permeate side
w_E^0	Mass fraction of ethanol in the initial liquid mixture
w_E^L	Mass fraction of ethanol in the liquid mixture after adsorption process
w_E^s	Mass fraction of ethanol adsorbed on silica xerogel
w_w^0	Mass fraction of water in the initial liquid mixture
w_w^L	Mass fraction of water in the liquid mixture after adsorption process
w_w^s	Mass fraction of water adsorbed on silica xerogel
x_{iR}	Molar fraction preferential component in retentate side
y_{iP}	Molar fraction of preferential component in permeate side
α	Selectivity
β	β-silicomolybdic acid

Symbol	**Definition**
η	Dynamic viscosity
ρL	Fluid density
ρs	Density of a ball (2.18685 $g.cm^{-3}$)
σ	Average area occupied by each molecule in the completed monolayer
τ	Time of proceeding the molybdate reaction

Introduction

The current environmental problems due to the continuous increase in the Colombian population as well as in the industrial development become also interesting subjects for chemical and material engineering. Therefore, through the research in this science fields is expected to propose alternatives to retrieve and counter the environmental imbalances.

One of the biggest environmental problems is the contamination by utilization of fossil fuels. It causes the degradation of natural resources and generation of diseases, having a negative effect on all living beings (Standeker et al., 2007). Two basic ways exist to face up the contamination problems. The first one consists of their treatment through technological applications to reduce negative effect of pollutants on the environment. Some of those techniques are ion exchange, membrane techniques, adsorption process, etc. The second one is based on the implementation of alternative energy sources to reduce the amount of emitted pollutants. It is well known that ethanol has been recognized as a potential, eco-friendly and economic substitute for petroleum based fossil fuels, contributing to the decrease in the greenhouse gas emission (Chovau et al., 2011; Ikegami et al., 2008). Its production engages few important steps, between them: fermentation, ethanol removal and purification. All of them involve alcohol-water mixtures at several concentrations. However, one of the most important requirements of ethanol to be applied as oxygenate for gasoline, is its dehydration degree (99.5%).

Traditionally removal and purification of ethanol is performed using a multi-column distillation system and adsorption system. However, the conventional methods for the separation of both azeotropic and close-boiling mixtures are complex, expensive and consume a large amount of energy. It has been estimated that ethanol removal and dehydration steps consume more than half of the total energy in the production of alcohol by fermentation (Kaewkannetra et al., 2011).

Membrane-based separation offers a simpler and more energy-efficient method, because the separation mechanism is independent of the vapor–liquid equilibrium characteristics of the mixture to be separated. Moreover, it is characterized with compact and modular design as well as the absence of the chemical agents required in many other separation processes (Chapman et al., 2008). Microporous inorganic membranes offer potential applications in gas/vapor/liquid separation. The major advantages of inorganic membranes, comparing to the polymeric ones, are their thermal, chemical and mechanical stability (Lin et al., 2002). Moreover, they present many operational advantages such as: long lifetime, high fluxes and wide range of operation parameters, despite their higher initial costs (Qianyao & Chunming, 2007). Two kinds of inorganic membranes that are used for the separation of small substances are especially important: hydrothermally synthesized zeolite membranes and sol–gel-derived silica membranes.

Silica-derived membranes are known since more than a decade (Uhlhorn et al., 1989). They can be used in many applications such as gas separation and pervaporation (Peters et al., 2005). Silica or silica-based membranes prepared using sol–gel techniques also are highly selective, while permitting high flux during pervaporation. An advantage of silica-based membranes is that they are relatively cheap (Peters et al., 2005). However, the hydrophilic nature of silica, related to the presence of silanol groups (Si-OH) on its surface, limits its practical application. It is well known that water can be adsorbed on silica via intermolecular hydrogen bonding between water molecules and silanol (hydroxyl) groups of silica, leading to its pore blocking and final membrane degradation (Wei et al., 2008). The replacement of hydrogen from the surface hydroxyl groups (Si–OH) with the hydrolytically stable alkyl or aryl groups (Si–R) through the oxygen bonds can prevent the adsorption of water resulting in hydrophobic material. The lack of commercial hydrophobic ceramic membranes gives to this subject special importance.

Therefore, the pervaporation, the separation of liquid mixture by partial vaporization through microporous silica membranes, appears to be a promising and economic process for ethanol removal (hydrophobic membranes) and purification (hydrophilic membranes). In these processes, separation of components (e.g. water and alcohol) is based on the difference in transport rate of individual components through the membrane (Chapman et al., 2008) and adsorption properties (Chen et al., 1998).

In addition, hydrophobic silicas are promising materials for purification of biologically active compounds and medicinal preparations as well as for stabilization of multicomponent systems. Due to the unique combination of properties, they can find also practical application as absorbents used in wastewater treatment, air purification, chemical purification, and column chromatography, acoustic insulators, catalysts support, among others.

Therefore, the aim of this thesis was to gain a more detailed insight into the different factors controlling the adsorptive properties of silica-derived xerogels. The influence of the physico-chemical properties on their performance as adsorbents of organic compounds (alcohols) and as materials for the preparation of inorganic membranes for ethanol removal and purification has been studied.

The realization of the intentional aim of thesis required:

- The preparation of hydrophilic and hydrophobic silica xerogels (powder materials) by the sol-gel method,
- The study of the physico-chemical properties of hydrophilic and hydrophobic silica xerogels (powder materials),
- The study of the effect of the preparation method and hydrophobic agent on the properties of the obtained hydrophobic silica xerogels (powder materials),
- The preparation of hydrophilic and hydrophobic silica membranes,
- The evaluation of the studied materials as adsorbents of organic compounds (specifically alcohols) and materials for preparation of inorganic membranes for ethanol removal and purification.

The characterization of the obtained materials consists of several sections:

- The textural and morphological properties using N_2 physisorption (*specific surface area, pore volume, pore size and pore size distribution measurements*), Scanning Electron Microscopy coupled with Energy Dispersive Spectrometer (*SEM-EDS*),
- The cristallinity degree using X-ray diffraction (*XRD*),
- The thermal stability using Thermo-gravimetric Analysis (*TGA-DTA-MS*),
- The surface characterization using Fourier Transform Infrared Spectroscopy (*FTIR*)
- The adsorption studies of different organic compounds, alcohols, (pure and/or in the aqueous mixture) in the liquid and gas phase by High-Performance Liquid Chromatography (*HPLC*) and Fourier Transform Infrared Spectroscopy (*FTIR*). The following alcohols were selected: methanol, ethanol, n-butanol and 1-pentanol. Methanol, ethanol and n-butanol were chosen due to their potential application as alternative fuel to petroleum; whereas 1-pentanol due to its relation with the ethanol production.
- The pervaporation experiments of ethanol-water mixtures.

Chapter 1.
Bibliographic study

Introduction

Silicon dioxide (SiO_2) is one of the most abundant components of the crust of the earth. Combined with the oxides of magnesium, aluminum, calcium, and iron, SiO_2 forms the silicate minerals in rocks and soil (Bergna, 1994). Silica is an interesting ceramic material in the field of materials science due to its low cost, availability and particular properties. Natural and synthetic silica has been used in the industry and engineering due to its interesting optical properties and other features such as thermal and electrical insulation, hardness and chemical stability.

Silica is used in a wide range of applications such as catalytic supports (Llorca et al., 1997), catalysts (Sohn et al., 1990), adsorbents (Esparza et al., 2005), polymeric additives (Ansarifar et al., 2005), glass nanocomposites with exceptional optical properties (Yeshchenko et al., 2008), etc. It has also played a key role since the beginning of civilization, first in flint for tools and weapons and in clay and sand for pottery. Moreover, the present technology could be very different without the silica used as the catalysts for oil refineries, the modern glass and ceramics, the electronic microcircuits, the quartz crystals, and the fiber optics (Bergna, 1994).

1.1 Silica gels

Silica gels are sol–gel derived porous materials. These materials are quite unique in the field of material science due to their specific properties including: high porosity (80-99%), high optical transmission (~90%), low sound velocity (~100 $m.s^{-1}$), low thermal conductivity (< 0.005 $W.m^{-1}K^{-1}$), low index of refraction (~1.05), low dielectric constant (~2) and extremely large specific surface area (500-1600 $m^2.g^{-1}$) (Gurav et al., 2009; Parvathy Rao et al., 2005a; Parvathy Rao et al., 2007; Soleimani Dorcheh & Abbasi, 2008). Due to such versatile and interesting properties, silica gels have been found several applications in the science and technology such as: Cerenkov radiation detectors (Carlson et al., 1979), superthermal insulators in solar energy systems, refrigerators and thermos flasks (Caps & Fricke, 1986), catalysts supports (Pajonk, 1991), thermal window insulations (Smith et al., 1998), acoustic barriers (Gross & Fricke, 1992), supercapacitors (Du et al., 2009), abrasive-polishing and flatting agent (Patterson, 1994), wastewater treatment material (Ahmed & Attia, 1995), membranes (Wei et al., 2008), adsorbents (Liu et al., 2009), cosmic dust capture (Tsou, 1995), bioencapsulator (Luckarift et al., 2004), biodegradable fibers (Podbielska & Ulatowska-Jarza, 2005) and carrier for drugs (Czarnobaj, 2008).

1.2 Synthesis of silica gel

Synthesis of silica gels by the sol-gel method involves three general steps: gel preparation, its aging and drying. The sol is prepared by hydrolysis of a silica precursor solution. The gel is achieved after condensation reaction of the formed sol. Next, the obtained gel is aged with the objective to become stronger, in order to avoid the shrinkage and collapse of gel structure during the drying process. Finally, in the last step (drying), the pore liquid is removed from the gel under specific conditions, in order to prevent collapse in the gel structure.

1.2.1 Gel preparation

The preparation of gels is still, in a great extent, an art, and many skills are required to achieve a specific final product (Gesser & Goswami, 1989). The sol-gel method is the most useful technique employed to silica gel preparation. It is a wet preparation method of ceramic materials with special characteristics in composition and physico-chemical properties.

The sol-gel process describes the transition of a liquid system, mostly colloidal, into a solid, gel phase. A sol is defined as a colloidal system of liquid character in which the dispersed particles are either solid and/or large molecules whose dimensions are in the colloidal range (1-1000nm). A gel is a colloidal system of solid character in which the dispersed substance forms a continuous, ramifying and consistent network which is interpenetrated by a fluid system (Gesser & Goswami, 1989). Gels are usually classified according to the applied dispersion medium: hydrogel or aquagel, alcogel, and aerogel for water, alcohol, and air, respectively (Soleimani Dorcheh & Abbasi, 2008).

1.2.1.1 Sol-gel method

The sol-gel method is a colloidal route used to synthesized ceramics with an intermediate stage including a sol and a gel state (Pierre, 1998). It has potential advantages over the other processes used to produce ceramic materials as chemical vapor decomposition (CVD) and hydrothermal process. The sol-gel method permits to obtain the new hybrid organic-inorganic materials which do not exist naturally. Glasses and ceramics with optimum microstructure, homogeneity and purity can be obtained using sol-gel method by hydrolysis and condensation of alkoxides at or near room temperature. In this method, the kinetics of various chemical reactions can be easily controlled by the low processing temperature and by the often dilute conditions. The nucleation and growth of the primary colloidal particles can also be controlled in order to obtain particles with a given shape and size distribution. Moreover, the distribution of the pores and crystalline or amorphous phase can also be tailored. Sol-gel method gives advantages for mixed oxides system in which chemical homogeneity is required (Kirkbir et al., 1996; Pierre, 1998).

In the specific case of silica gel preparation using the sol-gel process, it is possible to minimize the processing temperature and material losses during the synthesis of optical grade SiO_2 components. However, the biggest limitation of this method is still the cost of the precursors and specially that of alkoxides. For this reasons, sol-gel processing becomes much interesting for highly advanced materials (Pierre, 1998).

1.2.1.2 Silica precursors in the sol-gel method

The first step of any sol-gel process always consists of the precursor selection of the required materials. The precursors for the sol-gel process are metal or metalloid elements surrounded by various ligands. Metal alkoxides, belonging to the group of metal-organic compounds, are the class of precursor most commonly used in the sol-gel research due to their high reactivity with water. As a result of hydrolysis reaction, the hydroxyl ion becomes attached to the metal atom (Brinker & Scherer, 1990).

Silicon alkoxide (Venkateswara Rao et al., 2003) and sodium silicates (Shewale et al., 2008) are precursors mainly used for the preparation of silica gels by the sol-gel method. It should be noted that only alkoxide compounds are characterized with the high degree purity. However, their cost is higher comparing to the sodium silicates compounds (Pierre, 1998). In order to reduce the costs of raw materials, waterglass or sodiumsilicate solution can also be used as a silica source due to their lower price (Soleimani Dorcheh & Abbasi, 2008).

It should be noted that the nature of the precursor has a significant influence on hydrolysis and condensation rates as well as on the properties of the synthesized gel (Smirnova, 2002). Alkoxides precursors are recommendable to obtain high purity, homogeneous and small pore size silica gels. The alkoxide gels usually present pores smaller than 200 Ǻ (Kirkbir et al., 1996). The major drawback to employ alkoxides as a precursor is the problem of gel fracturing due to large shrinkage and enormous capillary forces during the drying process (Kirkbir et al., 1996; Yamane, 1988). It has been found that the hydrolysis rate of different silicon alkoxides decreases with an increase in the size of the alkoxy-group ($-OCH_3 > -OC_2H_5 > -OC_4H_9$). This could be attributed to the effect of steric hindrance in the hydrolysis reaction and to the decreased reactivity (Chen et al., 1986).

Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) are the alcoxides precursors commonly used in silica preparation. TMOS undergoes a more rapid hydrolysis than TEOS, producing narrow and uniform pores and higher surface area silica gels (Soleimani Dorcheh & Abbasi, 2008). However, the fumes liberated during the synthesis with TMOS are dangerous and can cause blindness. Moreover, TEOS precursor is cheaper than TMOS (Wagh et al., 1997). Other silicon alkoxides as methyltrimethoxysilane (MTMS) (Bhagat et al., 2007; Hegde & Venkateswara Rao, 2007; Venkateswara Rao et al., 2006; Venkateswara Rao et al., 2003b) and methyltriethoxysilane (MTES) (Aravind & Soraru, 2010; Jiang et al., 2008; Lanfang et al., 2004; Nadargi et al., 2009) are also used as silica precursor, especially in order to obtain flexible silica gels with good hydrophobicity (Nadargi et al., 2009). The MTMS and MTES silicon alkoxide contain one non-hydrolysable methyl group and three hydrolysable alkyl groups; methoxy groups for MTMS and ethoxy groups for MTES. Therefore the hydrolysable alkyl groups undergo hydrolysis and lead to the formation of monomeric units of the $–Si(OH)_3$ which are responsible for the formation of silica network (Nadargi & Venkateswara Rao, 2009). The sol–gel polymerization of MTMS and MTES leads to the formation of a three dimensional inorganic–organic network. The formed network remains open-ended on one side and gets connected on the remaining three sides. As a result, large pores are observed in the microstructure. The presence of such large pores and the CH_3 groups in the network are responsible for the elastic behavior of the MTMS and MTES based gels (Hegde & Venkateswara Rao, 2007).

1.2.1.3 Chemistry of the sol-gel method

The sol-gel method is based on hydrolysis of liquid precursors to form colloidal sols and their subsequent condensation to obtain the gel. The precursors are usually organosilicates (TEOS) yielding silicate sol-gel materials. However, the method is not restricted to the silicon compounds, for example compounds of zirconium, vanadium, titanium can be used as precursors leading to materials possessing different physico-chemical properties.

The synthesis of silica from tetra-functional alkoxides can be described by the following three general reactions: hydrolysis, water condensation and alcohol condensation, as presented in equations (1) to (3) , respectively.

$$\equiv\text{Si-OR} + \text{H}_2\text{O} \xrightleftharpoons[\text{esterification}]{\text{hydrolysis}} \equiv\text{Si-OH} + \text{ROH} \tag{1}$$

$$\equiv\text{Si-OR} + \text{HO-Si}\equiv \xrightleftharpoons[\text{alcoholysis}]{\text{alcohol condensation}} \equiv\text{Si-O-Si}\equiv + \text{ROH} \tag{2}$$

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \xrightleftharpoons[\text{hydrolysis}]{\text{water condensation}} \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \tag{3}$$

where R is an alky-group ($-C_xH_{2x+1}$).

In most cases, a catalyst, a mineral acid or a base, is employed. Since water and alkoxide do not mix sufficiently, alcohol is usually used as a solvent. In the hydrolysis reaction the replacement of an alkoxy group (OR) with a hydroxyl group (OH) takes place. Subsequently, the condensation reactions, involving the silanol groups (Si-OH), produce siloxane bonds (Si-O-Si) and as by-products alcohol (ROH) or water (Brinker & Scherer, 1990; de Lange, 1993). Further hydrolysis and condensation takes place using the products of reactions (1), (2) and (3) as reactants, in analogous reactions as presented above, initially leading to the oligomeric and polymeric structures.

Under most of conditions, condensation starts as soon as the alkoxy groups are hydrolyzed. The initial condensation rate is very high and short chains (or oligomers) are formed at this stage. At a later state, further condensation is possible only through the cross-linking of already formed chains, which are separated one from another by alcohols and water molecules. The cross-linking of these chains leads to the formation of a gel (Smirnova, 2002). Initially in the sol-gel process, dimmers and trimmers are formed and rapidly condense into cyclic siloxane (Si–O–Si) units, containing mostly four or six silicon atoms. The concentrations of terminal –OH and/or –OR groups depend on the hydrolysis and condensation kinetics and mechanisms, particularly determined by the nature of the applied catalyst (Fidalgo & Ilharco 2004).

Exists a pH, at which the rate of the condensation is the minimal; this point is near to the isoelectric point of silica. The isoelectric point of silica, at which the electron mobility and the surface charge is zero, occurs at approximately pH = 2 (McDonagh et al., 1996). In general, the rate of the condensation reaction is governed by the surface charge on the colloidal silica particles. Therefore, the condensation rate for silica is consequently quite low near to the isoelectric point, pH which silica surface charge is zero (Kijak, 2003). In contrast, at pH above the isoelectric point, the condensation reaction proceeds via a base-catalyzed mechanism. On the other hand, at pH below the isoelectric point, acid-catalyst mechanism is evidenced (Meixner & Dyer, 1999; Menon et al., 1998).

For more detailed description of the sol-gel process it is necessary to distinguish between processes under acidic and basic conditions, since solution pH affects the sol-gel process modifying the relative rates of hydrolysis and condensation as well as the reaction mechanisms. The value of pH, at which process under acidic conditions crosses to the basic one, is ca. 2, corresponding to the isoelectric point of silica.

1.2.1.3.1 Hydrolysis and condensation under acidic conditions

Hydrolysis of the alkoxide under acidic conditions (pH < 2) takes place via fast protonation, making the silicon more electrophilic and therefore more susceptible to attack by water in the second step (Figure 1- 1). However, protonation becomes slower when more hydroxyl-groups are present, since they are stronger electron-withdrawing, which affect the stability of transition state. Therefore, the hydrolysis rate decreases with extend in OH substitution (de Lange, 1993).

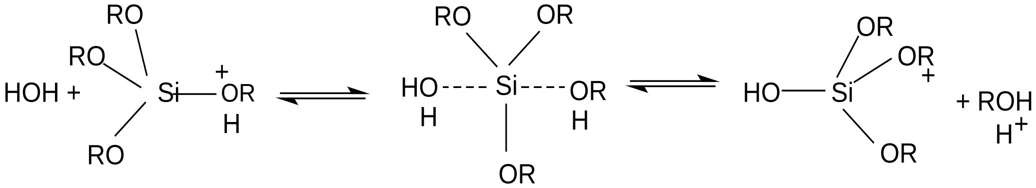


Figure 1- 1. Mechanism of the alkoxide hydrolysis under acidic conditions

Condensation reactions under acidic conditions take place via protonated silanol species (Si-HOR^+). These reactions are essentially irreversible since the rate of dissolution (siloxane bond hydrolysis) is low (Figure 1- 2)

They are much slower than the hydrolysis reaction and start generally when the hydrolysis process is almost complete. The constant of hydrolysis reaction rate k_H (reaction (1)), is 20 times higher than the constant of water condensation reaction k_W (reaction (2)), and at least 100 times higher than the constant of alcohol condensation reaction rate k_A (reaction (3)) (de Lange, 1993). One can see that hydrolysis and condensation under acidic conditions leads to the formation of the weakly branched gel, because their reactions rates are higher for less hydrolyzed and less branched system.

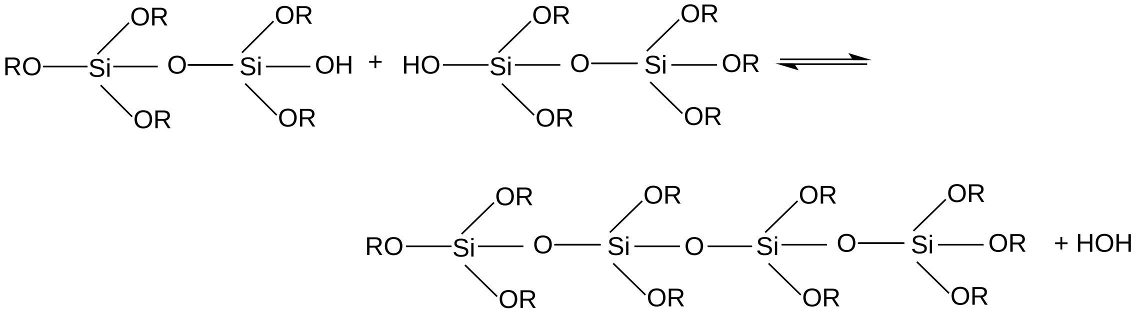


Figure 1- 2. Mechanism of condensation under acidic conditions leading to the formation of linear polymers

1.2.1.3.2 Hydrolysis and condensation under basic conditions

Hydrolysis of the alkoxide under basic conditions (pH > 2) takes place via dissociation of water in hydroxyl anions in a first rapid step. Next, an attack of hydroxyl ions on the silicon atom occurs (Figure 1-3) (de Lange, 1993).

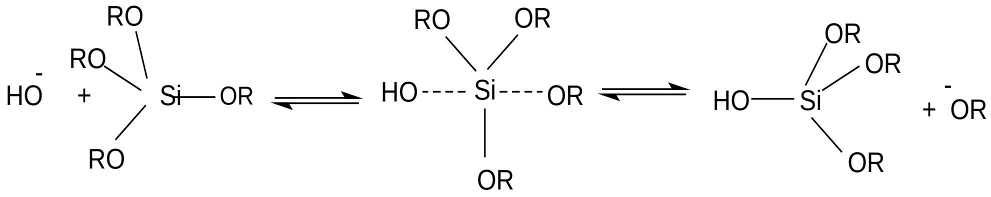


Figure 1-3. Mechanism of the alkoxide hydrolysis under basic conditions

Condensation reactions under basic conditions take place by attack of a nucleophilic deprotonated silanols (Si-O$^-$) on a neutral silicate species (Figure 1-4). The replacement of OH groups with the silicon atom by O-Si causes a reduced electron density on the Si, which increases the acidity of the protons on the remaining silanols. Therefore, condensation favors reactions between larger, highly condensed species, which contain acid silanols. For this reason, reaction rates under basic conditions are much higher than the hydrolysis reaction rates. They lead to the formation of large and highly crosslinked polymers. Moreover, gels formed from these large polymers contain large pores.

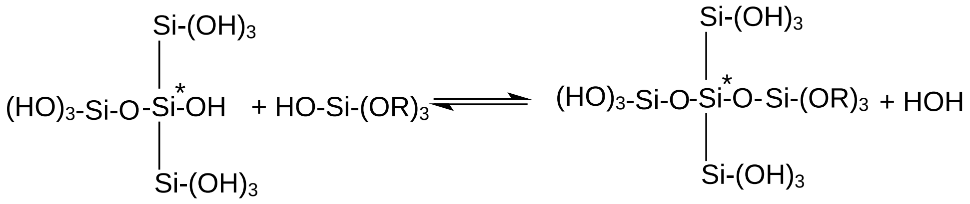


Figure 1-4. Mechanism of condensation under basic conditions leading to the formation of branched polymers

In general, there are also several parameters which influence the hydrolysis and condensation reactions under acid and basic conditions including the activity of the metal alkoxide, the alkoxide:water molar ratio, solution pH, temperature and nature of the solvent. Varying these processing parameters, materials with different microstructures and surface chemistry can be obtained (Gurav et al., 2010; Meixner & Dyer, 1999).

The specific reactions of silica gel preparation using TEOS as silica precursor are presented in equations (4) to (6):

$$Si(OC_2H_5) + 4H_2O \rightleftharpoons Si(OH)_4 + 4C_2H_5OH \tag{4}$$

$$Si(OH)_4 + (OH)_4Si \rightleftharpoons (OH)_3\text{-}Si\text{-}O\text{-}Si(OH)_3 + H_2O \tag{5}$$

$$Si(OH)_4 + (OC_2H_5)_4Si \rightleftharpoons (OH)_3\text{-}Si\text{-}O\text{-}Si(OC_2H_5)_3 + C_2H_5OH \tag{6}$$

The concentrations of hydroxyl groups (–OH) on silica surface depend on the hydrolysis and condensation kinetics and mechanisms, particularly determined by the nature of the applied catalyst. Considering that TEOS hydrolysis and condensation reactions are completed, the global reaction of silica synthesis can be presented as follows:

$$n\mathrm{Si(OC_2H_5)_4} + 2n\mathrm{H_2O} \longrightarrow n\mathrm{SiO_2} + 4n\mathrm{C_2H_5OH} \tag{7}$$

Actually, complete hydrolysis and condensation reactions never take place, and wet gel can contain a significant remaining amount of silanol (Si–OH) groups at the surface. They may undergo further condensation upon ageing and drying processes (Brinker & Scherer, 1990; Fidalgo & Ilharco, 2004).

If the trifunctional organosilane compounds as MTMS or MTES are used as precursor of silica gel, the hydrolysis and condensation reactions can be presented as follows (Figure 1-5 and Figure 1-6) (Bhagat et al., 2007; Nadargi & Venkateswara Rao, 2009):

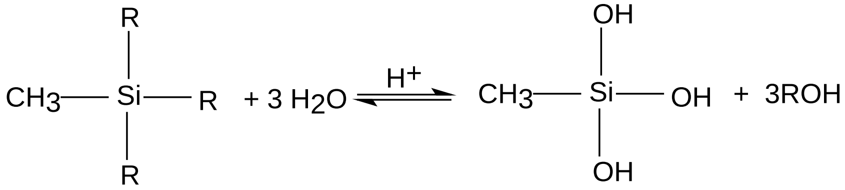


Figure 1-5. Scheme of hydrolysis of tri-functional alkoxide

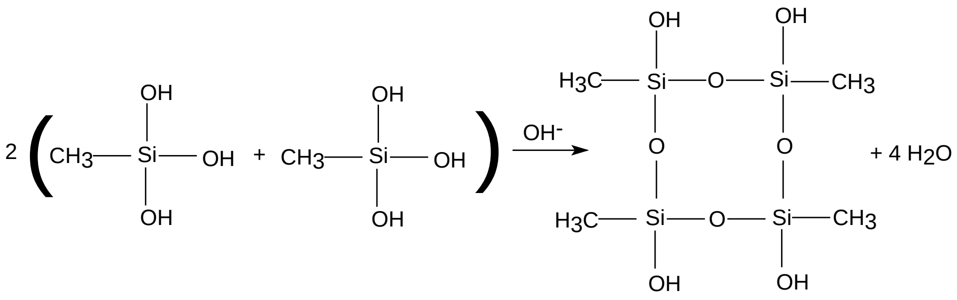


Figure 1-6. Scheme of condensation of trifunctional alkoxide

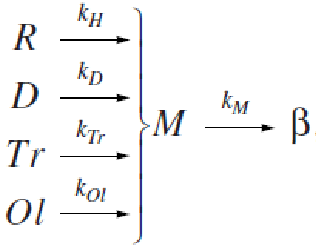
1.2.1.4 Kinetics of sol-gel method

Several authors have been investigated the kinetics of sol-gel method using diverse experimental techniques such as: nuclear magnetic resonance spectroscopy (^{29}Si NMR) (Assink & Kay, 1991; Devreux et al., 1990; Mazúr et al., 1999; Sefcik & McCormick, 1997), small angle X-ray scattering (SAXS) (Devreux et al., 1990) and spectrophotometric technique (molybdate method) (Rakhimov et al., 2008; 2009).

Nuclear magnetic resonance (NMR) provides chemical information at the atomic scale on the initial stages of the hydrolysis and condensation of silica, whereas small-angle radiation scattering characterizes the geometrical arrangement in the 1-1000 nm range at the final stage of the hydrolysis and polymerization process (Devreux et al., 1990).The application of molybdate method to determine the silicon under dynamic conditions of the hydrolysis and condensation, let to know the total amount of weakly structured (oligomers) and strongly structured (polymers) species of silica (Rakhimov et al., 2009).

Rakhimov et al. (1999) developed the molybdate method; spectrophotometric technique for determining the kinetic characteristics of the molybdate reaction, which represents the interaction between weakly structured species of silica (monomers, dimers, and linear trimers) and molybdate ions. At the initial time of the molybdate reaction, the following molecular species are presented: (1) unhydrolyzed species (R), which contain Si–O–R bonds (R is alkyl group), these species are assumed to be monomer alkoxysilane molecules. (2) low-molecular species which include monomers ($Si(OH)_4$, M), dimers ($Si_2O(OH)_6$, D), and trimers ($Si_3O_3(OH)_6$, Tr). (3) high-molecular weakly structured species: oligomers (Ol) which contain more than three silicon atoms and are decomposed under the action of the ammonium molybdate with the formation of β-silicomolybdic heteropoly acid. (4) high-molecular strongly structured species: polymers (P), which are not decomposed under the action of the molybdate reactant.

In order to analyze quantitatively the kinetics of formation of β-silicomolybdic acid,the reaction proposed by Rakhimov et al. (2009) can be considered.



(8)

Where:
R: Unhydrolyzed species
D: Dimers
Tr: Trimers
Ol: Oligomers
M: Monomers
β: β-silicomolybdic acid
k: Reaction rate constant

The presented reaction scheme is based on the facts that the molybdate ions interact only with the monomer species ($Si(OH)_4$ particles). The other particles should be transformed into the monomer species to react with molybdate reagent (Rakhimov et al., 2009). Therefore, the kinetic scheme of the molybdate reaction can be represented as a multistage reaction that involves the stages of the decomposition of unhydrolyzed species, the dissociation of weakly structured associates, and the interaction of molybdate ions with Si–OH bonds.

According to the kinetic scheme (8), the reactions of monomers formation can be represented as first-order reactions and their kinetic equations can be presented as follows:

$$\frac{d[R]}{d\tau} = k_H[R] \tag{9}$$

$$\frac{d[D]}{d\tau} = k_D[D] \tag{10}$$

$$\frac{d[Tr]}{d\tau} = k_{Tr}[Tr] \tag{11}$$

$$\frac{d[Ol]}{d\tau} = k_{Ol}[Ol] \tag{12}$$

Where :
k: Rate constant of the first-order reaction
$[R]$: Alkoxide concentration
$[D]$: Dimers concentaration
$[Tr]$: Trimers concentaration
$[Ol]$: Oligomers concentaration
τ:Time of proceeding the molybdate reaction

The transformation of M into β can be treated as a first-order reaction with the rate constant k_M. The time dependence of monomer concentration is described by the equation (13).

$$\frac{d[M]}{d\tau} = k_H[R] + k_D[D] + k_{Tr}[Tr] + k_{Ol}[Ol] - k_M[M] \tag{13}$$

The amount of polymers in the system is calculated as the difference between the total silica content (total amount of the initial alkoxide) and the total content of weakly structured silica at a given instant of time (Rakhimov et al., 2008).

The solution of differential equation system, gives the concentration of weakly and strong structured silica species at a given instant of time. In calculations are used the hydrolysis and molybdate reaction rate constants and dissociation rate constants calculated for dimmers and trimers from the data available in the literature (Rakhimov et al., 2009). The actual weight fractions of molecular species of silica are calculated as it is presented in equations (14)-(20)

.

$$X_R = \frac{[R]}{[Si]_0} \tag{14}$$

$$X_D = \frac{[D]}{[Si]_0} \tag{15}$$

$$X_{Tr} = \frac{[Tr]}{[Si]_0} \tag{16}$$

$$X_{Ol} = \frac{[Ol]}{[Si]_0} \tag{17}$$

$$X_P = \frac{[P]}{[Si]_0} \tag{18}$$

$$X_M = 1 - X_R - X_D - X_{Tr} - X_{Ol} - X_p \tag{19}$$

$$[Si]_O = [R]_O + [D]_O + [Tr]_O + [Ol]_O + [P]_O + [M]_O \tag{20}$$

The change of weight fractions of molecular species during the hydrolysis and condensation of TEOS varying the pH value and at Si:H_2O of 1:6 are presented in Figure 1-7.

The scheme of the acid-catalyzed hydrolysis and condensation (pH=2) can be represented in the form of four stages: (i) the rapid hydrolysis of the alkoxide with the formation of monomers, (ii) the slow association of monomers with the formation of dimers and trimers, (iii) the rapid association of dimers and trimers with the formation of oligomers and polymers, and (iv) the slow interaction of high-molecular species with each other and monomers with subsequent gelation.

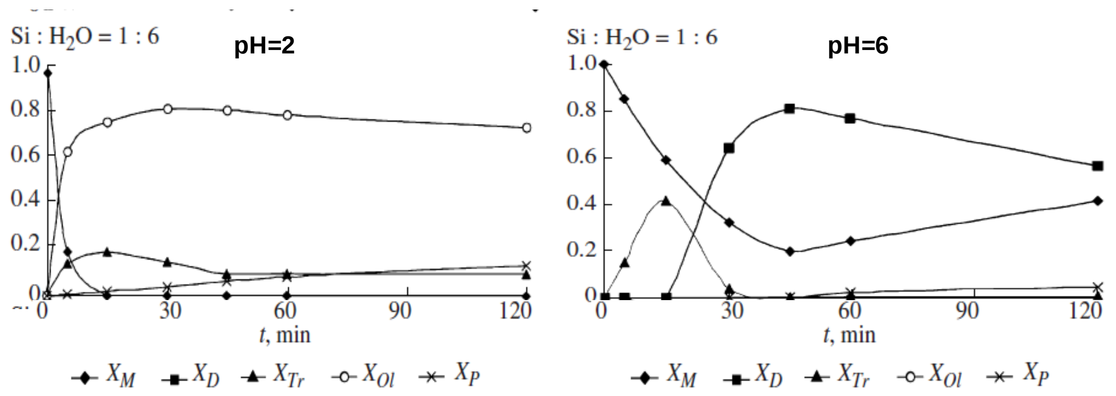


Figure 1-7. Weight fractions of molecular species of silica during the hydrolysis and condensation of TEOS.

In the case of the base-catalysed hydrolysis and condensation (pH =6), the slow hydrolysis of alkoxide with the slowly formation of monomers and trimers could be observed. At times up to 20 min., a decrease in the number of monomers and trimers is observed, due to the increase in the fraction of dimmers (Tr + M → 2D) Subsequently, the fraction of dimers decreases, which is accompanied by an increase in the fraction of monomers. Therefore, the species formed in the hydrolysis are gradually decomposed, as a result of reverse reactions.

The presence of oligomers in acid-catalysed silica generates weakly branched and microporous silica structure. The lack of oligomers on base-catalysed silica and the presence of high amounts of dimmers and polymeric species cause the formation of branched and uniform silica gel structures which presents high pores size.

1.2.2 Aging process of silica gels

The chemical evolution of the gel also continues after the gelation. This post-gelation process is known as aging (Smirnova, 2002). During aging, the strength and stiffness of the wet gel is improved, therefore the linear shrinkage during drying is kept to a minimum. Also, during long aging process, the particle and pore size usually are increased and homogenized (He et al., 2009).

The wet gel may be strengthened through aging by syneresis and Ostwald ripening mechanism (Soleimani Dorcheh & Abbasi, 2008). The syneresis is characterized with shrinkage of the gel network, caused by further condensation reactions. On the other hand, the ripening is a process of dissolution and re-precipitation driven by differences in the solubility between silica particles. The smaller particles present higher solubility leading to their precipitation and formation of the larger ones. The presence of larges particles causes the decrease in the interfacial area and the increase in average pore size (Kirkbir et al., 1996; Meixner & Dyer, 1999; Smirnova, 2002).

According to the literature (He et al., 2009), several conditions have been used for aging process. The aging conditions have a strong influence on the textural properties of silica gel. The aging of the wet gel in alcoholic solutions containing the silica precursor causes the hydrolysis, condensation and precipitation of the added monomers/oligomers onto the gel network. This process increases the stiffness of the silica network by adding new monomers and improving the degree of siloxane cross linking, without drastic modifications in the pore size (Fidalgo & Ilharco

2005). The aging of the gel in a TEOS/ethanol mixed solution, at high temperature and pressure, can promote the dissolution and reprecipitation of silica, further hydrolysis and condensation of unhydrolyzed $\equiv$Si–O–C_2H_5 groups, and the esterification of silanols, which will enhance the backbone strength of silica gel (He et al., 2009; Soleimani Dorcheh & Abbasi, 2008). The aging of the wet gel in an aqueous solution can promote the dissolution and reprecipitation of small silica onto the contact point of particles, which will increase the neck area and thus enhance the skeletal strength of silica gel (He et al., 2009). It enlarges the mechanical stability of silica gels and leads to the decrease in the external and microporous surface area (Soleimani Dorcheh & Abbasi, 2008). It should be noted that high water concentration in aging solutions causes faster shrinkage and stiffening of the gels (Kirkbir et al., 1996).

It is also possible to realize the aging of the gel in the original pore liquid, which is mainly composed with water and ethanol. It usually improves the strength and stiffness of the wet gel by rebuilding the network via further hydrolysis, condensation and specific reaction of these monomers. Other way to increase the gel strength is aging in ethanol at room temperature, longer time is required to realize the complete dissolution and reprecipitation of silica, otherwise, if these processes are incomplete will result in the weak backbone of wet gel (He et al., 2009). Gels can be also aged in more aggressive condition such as ammonia solution, nevertheless it increases considerably the micropores volume (Soleimani Dorcheh & Abbasi, 2008).

It has been determined that the aging time and aging temperature have influence on the properties of the final material. Prolonging the aging time can increase the skeletal strength of silica gel while increasing the aging temperature can shorten the aging period (He et al., 2009). Short aging times cause the formation of the cracked gels. Longer aging times make the entire process of silica synthesis less feasible economically (Kirkbir et al., 1996).

1.2.3 Drying process of silica gels

The process of removing the majority of pore liquid from the gel is called drying (Gurav et al., 2010). If the solvent is removed at supercritical conditions an aerogel is obtained. On the other hand, if the solvent is removed by conventional thermal treatment a xerogel is produced (Gonzáles-Hérnandez, Pérez-Robles, Ruiz, & J.R Martínez, 2000).

Drying is the last critical step of a silica gel preparation. It can be divided in three general stages. The first one occurs while the gel is still immerse in liquid, and corresponds to an approximately constant solvent evaporation. The second one starts when the gel becomes exposed to the atmosphere and drying occurs by solvent flux to the surface, causing a continuous decrease in the rate of mass loss. Finally, the last one consists of the solvent evaporation from the gel, followed by diffusion towards the surface (Fidalgo & Ilharco, 2005).

During drying process, stress builds up, shrinkage as well as cracking of the gel network occurs due to capillary forces that set up in the pores by the liquid vapor interfaces (Gurav et al., 2010). Shrinkage takes place until capillary pressure is resisted by the modulus of the solid network. The extent of gel shrinkage depends on many factors such as pore size and pore size distribution (Parvathy Rao et al., 2005a). The presence of small pore size can induce fracture during the drying process due to enormous capillary forces. It is known that the pore liquid is under enormous tension when the pore size is smaller than 200 Ǻ (Soleimani Dorcheh & Abbasi, 2008). Capillary force in the gel is proportional to the evaporation rate and inversely proportional to the pore size. During the initial stage of drying, capillary forces are big and provoke high evaporation rate. During the final stages of drying, the rate of evaporation is small, however the pore size is already considerably reduced and fracture causing capillary force can occur (Yamane, 1988). To prevent the collapse of the gel structure, drying must be made under special conditions.

Traditionally, silica aerogels have been dried using supercritical drying (SCD) methods based on the pore liquid removal above the critical temperature and pressure of the solvent. At this point, liquid–vapor interface as well as capillary pressure does not exist. However, it should be noted that those techniques present certain limitations in terms of their cost, efficiency, process continuity, and safety, considering that high-temperature (250–270°C) and pressure (8–10 MPa) are needed to approach the critical point (Gurav et al., 2010; Parvathy Rao et al., 2005b).

There are two different ways to realize supercritical drying, under high (HTSCD) or low temperature (LTSCD) conditions (Soleimani Dorcheh & Abbasi, 2008). The HTSCD method was the first one proposed to dry silica gel and is still widely used. The wet gel, together with a sufficient amount of solvent is placed in an autoclave, at which the temperature is slowly increased, causing an increase in the pressure. Temperature and pressure are adjusted above the critical points of the corresponding solvent and kept constant a certain period of time. Then, the fluid is slowly vented at constant temperature, resulting in a pressure drop to ambient pressure. In the LTSCD method, the solvent present in the gel is replaced by liquid CO_2 which has the critical point close to the ambient temperature. Usually this technique works at low temperature (< 40 °C) and moderate pressure (< 80 bar), similarly to the HTSCD. The HTSCD and LTSCD are considerably expensive due to the high pressures involved. For this reason there is a great interest in subcritical or ambient pressure drying. These approaches offer a great promise to decrease the costs of silica gel preparation, representing an important consideration for the future development of these materials (Soleimani Dorcheh & Abbasi, 2008).

During the gels drying at ambient pressure, surface tension between liquid and vapor cannot be avoided and irreversible shrinkage occurs until the capillary pressure is resisted by bulk modulus of the gel (Parvathy Rao et al., 2005b). The irreversible shrinkage is provoked by the presence of hydroxyl (OH) and/or alkoxy (OR) groups in the gel. As a consequence of the drying process, those surface groups can react to form Si-O-Si bonds via water or alcohol condensation, provoking the collapsing of the gel structure (Parvathy Raoet al., 2005a). In order to avoid it, the reduction of the capillary pressure by increasing the pore size of the gel, the exchange the pore liquid with solvents and modification of the silica surface are considered. Therefore, silica pore size can be increased using basic catalyst in the sol-gel process, producing gels with highly branched structure and larger pores and pores volume (Smirnova, 2002). The solvent exchange is done to replace the pore liquid with a solvent with low surface tension and vapor pressure to reduce the shrinkage of the gel during drying (Parvathy Rao et al., 2007). The physical properties of the silica gels depend on the surface tension and vapor pressure of the applied solvent, as well as on its molecular weight. The exchanging of pore liquid with solvents characterized with high molecular weight and long chain produces silica gels with low density, high percentage of porosity and high pore volumes.

Protic solvents such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol and hexanol have been used to exchange the pore liquid before drying. Some of them take part in the condensations reactions and their presence in the pores also affects the aging occurring during drying. Therefore, the use of aprotic solvents such as hexane, cyclohexane, heptane, benzene and toluene, which do not take part in the aging reactions, might have been a better approach in the solvent exchanging (Kirkbir et al., 1994). The solvents heptane and xylene characterized with low surface tension produce less capillary force and less shrinkage gels during drying (Parvathy Rao et al., 2005b).

Surface modification of the gels through the replacement of H from Si–OH groups by non-polar alkyl or aryl groups is a crucial step in the ambient pressure drying method. Several hydrophobic reagents as methyltrimethoxysilane (MTMS), hexamethyldisilazane (HMDZ) and trimethylchlorosilane (TMCS) have been employed to alter the wetting properties of the silica surface (Gurav et al., 2010).

Alkoxide gels are difficult to dry rapidly without fracture. Drying of wet gels must be done very carefully, particularly when carried out by the simple evaporation of solvent, in order to avoid the stress build up due to high evaporation rate (Yamane, 1988). Very slow heating and cooling rates of 0.5°C and isothermal dried at specific temperatures are usually used to prevent gel collapse (Yamane, 1988).

Heat treatment can be also used for gel densification. Silica densification is usually carried out at the temperature range from 600 to 1200°C. In this temperature range, gel partially becomes more dense and finally porous silica glass is formed. The structural change of the silica skeleton during heat treatment is attributed to the development of crosslinking of the Si-O bonds, as a consequence of the condensation reactions of silanols (Venkateswara Rao et al., 1999).

1.3 TEOS:ethanol:water:nitric acid molar ratio

It is well known that the research in materials science is base on the experimentation and the practical experience in the synthesis and characterization of materials, instead of predictive models or simulations of those process. Therefore the selection of more appropriate conditions of sol-gel method is supported by the previous studies of several authors in the field of silica gels.

In this research, TEOS is selected as silica precursor because of its low cost and low toxicity in comparison with other alkoxides compounds. Ethanol is the appropriate solvent widely used to dissolve alkoxisilanes like TEOS; for this reason, it was used in this study.

According to the literature, the synthesis conditions which lead to weakly branched system with small pore size involve the application of an acid catalyst (pH < 2) and low and/or moderate quantity of water (TEOS:water molar ratio less than to 1:10) (de Lange et al., 1995). Nitric acid is an inorganic acid which permits to obtain a uniform, small and narrow pore size distribution in the gel. It is a safety acid that was chosen to be used in the preparation of silica xerogels by the sol-gel method.

According to de Lange et al. (1995) and Uhlhorn et al. (1992) the application of standard molar ratio TEOS:ethanol:water:nitric acid of 1:3.8:6.4:0.085, respectively let to obtain microporous silica gels ($D_{poro} < 2\,nm$) characterized with a weakly branched polymeric structure. The TEOS:ethanol molar ratio of 1:3.8 guarantees complete miscibility of silica precursor in the solvent, due to their equal volumetric amounts. The TEOS:water molar ratio should be chosen carefully to obtain the gel with the required properties. The TEOS:water molar ratio of 1:6.4 ensures high hydrolysis rate and microporous silica gels, avoiding the higher dilution of reaction species during the reaction. Finally, TEOS:nitric acid molar ratio of 1:0.085 permits accelerate hydrolysis reaction to obtain silica gels with low pore size.

In this study, the standard molar ratio TEOS:ethanol:water:nitric acid was employed to obtain silica xerogels with small pore size and narrow and uniform pore size distribution.

1.4 Weak points of silica gels

Silica gels have exceptional thermal, acoustic, optical, adsorptive and catalytic properties (Venkateswara Rao & Kalesh, 2004). However, some of its weak points are also already well known: fragility, collapse of gel structure due to adsorption of moisture from the humid surroundings and the material deterioration with the time (Venkateswara Rao et al., 2007; Venkateswara Rao et al., 2004).

Traditional silica gels based on TEOS and TMOS precursors are inherently hydrophilic in nature due to the presence of Si–OH groups on its surface. Silica surface carries on an average 4–6 hydrolyzable silanol (Si-OH) groups per nm^2; therefore, the surface exhibits hydrophilic properties (Hegde et al., 2007). Those groups can take part in hydrogen bonding with H_2O, promoting the adsorption of water on the silica surface (Standeker et al., 2007; Venkateswara Rao et al., 2003a) and limiting its applications. In order to extend its range of possible applications, the chemical modification of its surface can be considered. The replacement of the H from the surface hydroxyl groups (Si–OH) with the hydrolytically stable alkyl or aryl groups (Si–R) through the oxygen bonds can prevent the adsorption of water and hence results in hydrophobic silica surfaces (Latthe et al., 2009; Venkateswara Rao & Kalesh, 2004; Wagh & Ingale, 2002). The schematic representations of hydrophilic and hydrophobic silica gels are presented in Figure 1-8.

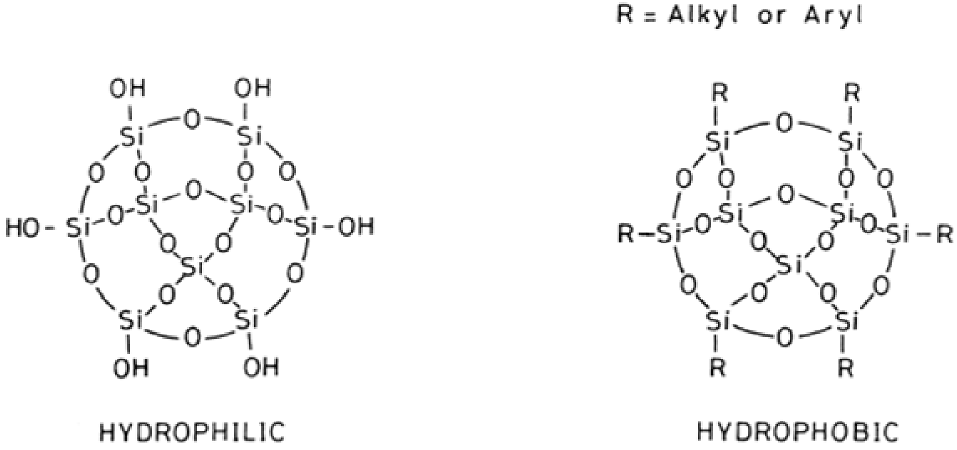


Figure 1-8. Schematic diagram presenting hydrophilic and hydrophobic surface of silica gels (Venkateswara Rao & Huranath, 1999)

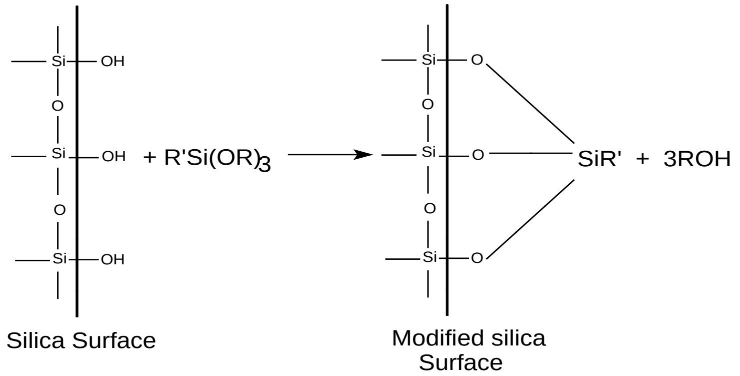
1.5 Chemical modification of silica gel

Chemical modification of silica surface relates to the processes that lead to change in chemical composition of the surface. Surface can be modified either by physical treatment (thermal or hydrothermal) that leads to change in ratio of silanol and siloxane concentration of the silica surface or by chemical treatment that leads to change in chemical characteristics of silica surface (Jal et al., 2004).

Silica gel surface can be modified by organofunctionalization, where the modifying agent is an organic group, and inorganofunctionalization, in which the group anchored to the surface, can be an organometallic composite or a metallic oxide. Organically modified silicas are considered to be promising materials with new properties. The sol gel method is the only preparation technique giving possibility to introduce organic molecules into inorganic network on the molecular level. Through the modification of silica surface is possible to change its physical and chemical properties in a controlled way (Nocun et al., 2005). The modified silica can be applied in the following areas (Vansant et al., 1993):

- Analysis: adsorbents in gas and liquid chromatography (GC and HPLC), wastewater and air purification
- Chemistry: heterogeneous catalyst in several nucleophilic reactions (Jin & Kurus, 1992), catalysts support
- Biochemistry: enzyme immobilization
- Industrial: sensors to monitor air pollution emissions, membranes

If the appropriate surface chemical modification is made, the surface of silica gel can become hydrophobic, and the water molecules will be repelled (Venkateswara Rao & Bhagat, 2006). The hydrophobicity of the gels can be achieved by two methods: surface chemical modification of the gel by gaseous reagents (Leboda, 1978) and surface modification of colloidal particles by the incorporation of certain chemical additives in the alcosol (Venkateswara Rao & Pajonk, 2001). The last method is based on the substitution of the hydrogen of the OH group with some organic groups (alkyl or aryl). It can be achieved by the addition of organosilane surface modifiers alkylalkoxysilanes, alkylsilazanes or alkylchlorosilanes (type R_nSiX_{4-n}) since they have at least one hydrolyzable group along with one or more non-hydrolyzable groups. Since Si–OR or Si–Cl group is hydrolyzable, it can react with the OH groups, making the surface hydrophobic (Venkateswara Rao et al., 2007). The general reaction of silica surface modification can be written as follows (21):



(21)

where R’ are methyl (CH_3), ethyl (C_2H_5) or phenyl (C_6H_5) groups and R are methyl (CH_3) or ethyl(C_2H_5) groups.

In the majority of cases the reactions realized with the participation of silica surface sites are classified as the heterolytic processes of substitution, addition, elimination or rearrangement. In a wide group of reactions, the attack is realized by an electrophilic reagent to an oxygen atom of a surface silanol group. It includes the reaction of electrophilic proton substitution (SEi) at interaction with different chloro- and alkoxysilanes, organosilazanes and various organometallic compounds, and also the processes of electrophilic addition (AdE). For instance, the interaction of trimethylmethoxysilane and ethyleneimine with surface silanol groups represents a typical example of a reaction proceeding according to mechanisms SEi and AdE, respectively (Auner & Weis, 1998).

Various techniques have been used for the organic surface modification of the silica aerogels from the corresponding monomer, between them: co-precursor and derivatization methods (Venkateswara Rao & Kalesh, 2004). The co-precursor method, proposed by Schwertfeger et al. (1994), is based on the addition of the hydrophobic reagent to the alcosols prepared using silica precursor (TMOS or TEOS) to obtain hydrophobic silica aerogels. On the other hand, in the derivatization method, (Yokogawa & Yokoyama, 1995) the alcogel prepared using TMOS or TEOS is immersed in a chemical bath containing the hydrophobic reagent and a solvent (methanol or ethanol). Then a solvent exchange is made to remove unreacted substances to obtain finally a hydrophobic material (Venkateswara Rao et al., 2004).

Table 1-1 lists silica precursors and some mono-, di- and tri-functional hydrophobic agents which have been used as hydrophobicity source of silica aerogels. Figure 1-9 presents the structure of some of them.

Table 1-1. Hydrophobic agents employed in co-precursor and derivatization method to obtain hydrophobic silica aerogels

Hydrophobic Agent		References
DMCS	Dimethylchlorosilane	(Venkateswara Rao & Kalesh, 2004; Venkateswara Rao et al., 2003a)
DMDC	Dimethyldichlorosilane	(Venkateswara Rao & Bhagat, 2006)
DMDS	Dimethyldiethoxysilane	(Venkateswara Rao & Bhagat, 2006)
ETES	Ethyltriethoxysilane	(Venkateswara Rao & Bhagat, 2006; Venkateswara Rao et al., 2007)
HDTMS	Hexadecyltrimethoxysilane	(Latthe et al., 2009)
HMDSO	Hexamethyldisiloxane	(Wang & Zhao, 2009)
HMDZ	Hexamethyldisilazane	(Gurav et al., 2009; Parvathy Rao et al., 2005a; Venkateswara Rao et al., 2003a)
MTES	Methyltriethoxysilane	(Jeon et al., 2002; Lanfang et al., 2004; Venkateswara Rao & Kalesh, 2004)
MTMS	Methyltrimethoxysilane	(Nocun et al., 2005; Standeker et al., 2007; Venkateswara Rao et al., 2004)
PrTMS	Propyltrimethoxysilane	(Venkateswara Rao & Bhagat, 2006)
PTES	Phenyltriethoxysilane	(Parvathy Rao et al., 2005c; Venkateswara Rao & Bhagat, 2006; Venkateswara Rao et al., 2007)
PTMS	Phenyltrimethoxysilane	(Venkateswara Rao & Bhagat, 2006)
TMBS	Trimethylbromosilane	(Venkateswara Rao & Bhagat, 2006)
TMCS	Trimethylchlorosilane	(Jeon et al., 2002; Shewale et al., 2008; Venkateswara Rao & Bhagat, 2006)
TMES	Trimethylethoxysilane	(Hegde et al., 2007; Standeker et al., 2007; Venkateswara Rao et al., 2004)
TMMS	Trimethylmethoxysilane	(Venkateswara Rao & Bhagat, 2006)
TMS	Tetramethylsilane	(Venkateswara Rao & Bhagat, 2006)
TMSCA	Trimethylsilylchloroacetate	(Venkateswara Rao & Bhagat, 2006)
VTES	Vinyltriethoxysilane	(Jeon et al., 2002)
VTMS	Vinyltrimethoxysilane	(Jeon et al., 2002)

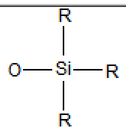
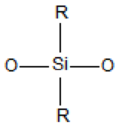
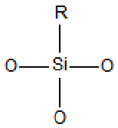
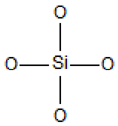
Units	**Monofunctional**	**Difunctional**	**Trifunctional**	**Quadrifunctional**
Structure				
Silicon oxide content	$SiO_{0.5}$	SiO_1	$SiO_{1.5}$	SiO_2
R/Si ratio	3	2	1	0
R_nSiX_{4-n}	TMCS, HMDZ	DMCS	MTMS,PTES	TEOS,TMOS

Figure 1-9. Structure of silica precursors and hydrophobic agents used for silica aerogel modification (Venkateswara Rao et al., 2004)

Monolithic and transparent hydrophobic silica aerogels are obtained using MTES and MTMS co-precursors, PTES, TMES, ETES, and HMDZ modified aerogels are monolithic and opaque, and DMCS and TMCS modified aerogels are cracked and opaque (Venkateswara Rao & Kalesh, 2004). The silica aerogels modified with MTMS and MTES are more transparent compared to the other co-precursors, which is due to the fact that the methyl group is smaller compared to the other alkyl or aryl groups.

Silica aerogels modified with TMES and HMDZ resulted to be more hydrophobic in comparison with those prepared with MTMS or MTES. It is related to the R/Si ratio; the larger R/Si ratio is, more hydrophobic material is (Venkateswara Rao et al., 2004). The superhydrophobic silica has been obtained by Venkateswara Rao et al. (2009) using MTMS as silica precursor and TMCS and HMDZ as hydrophobic agents during silica aerogel modification.

As far as verified, no research over organic surface modification of silica xerogels has been reported.

1.6 Conclusions of bibliographic study

- Silica gels are sol–gel derived nanoporous materials. Due to their specific properties such as: high porosity, extremely large specific surface area, etc. they have been found several applications in the science and technology: catalysts and catalysts support, adsorbents in wastewater and air treatment, adsorbents in column chromatography, membranes, etc.

- The synthesis of silica gels involves three specific steps: gel preparation, aging and drying process. The properties of the gel obtained are related to the conditions used in each step. To obtain silica xerogel with a small pore size and high specific surface area the application of the standard molar ratio TEOS (1) : ethanol (3.8) : water (6.4) : nitric acid (0.085) in the sol-gel process, and gel drying at atmospheric pressure are required.

- Aging process produces the strengthening of the gel to avoid the shrinkage and collapse of weak gels during drying process. Silica xerogels synthesized under acidic conditions present higher shrinkage in comparison with those obtained under basic ones due to the formation of weak silica network at pH lower than silica isolectric point.

- The hydrophilic nature of silica xerogels limits their practical application. Silica xereogel can be deteriorated by the water adsorption by intermolecular hydrogen bonding between water molecules and silanols groups presents on silica surface. Chemical modification of silica by replacement of H from silanol groups by methyl or aryl groups confers hydrophobic properties to silica surface avoiding the water adsorption.

- Chemical modification gives to silica new properties and new possible applications such as sensor, membranes, adsorbents in gas and liquid chromatography, heterogeneous catalyst, etc. Several hydrophobics agents have been used as co-precursor and derivatization agent in silica aerogels modification. MTMS and MTES are considered the two hydrophobic agents which produce transparent silica aerogel with small pore size. Moreover, so far there is no published study related to the chemical modification of silica xerogels.

Chapter 2.
Experimental study

Introduction

The synthesis procedures used for the preparation of hydrophilic and hydrophobic silica xerogels, versatile materials which can be applied in the adsorption of organic compounds as well as the production of inorganic silica membranes are presented. Physico-chemical, thermal, structural, textural, morphological and adsorptive properties of those materials were studied using different techniques available in the Universidad Nacional de Colombia, Sede Manizales and the Technical University of Lodz, Poland, in order to understand their performance in the potential practical applications as adsorbent material and membranes. Consequently, device specificities of the applied materials and methods are elucidated below.

2.1 Purity of reagents

Table 2-1 summarizes the chemical reagents and gases used during the preparation and characterization of hydrophilic and hydrophobic silica xerogels materials as well as silica membranes.

Table 2-1. Chemical reagents and gases used during preparation and characterization of silica xerogels

Reagent	Chemical Formula	Purity	Provider
Tetraethyl-orthosilicate (TEOS) for synthesis	$C_8H_{20}O_4Si$	> 99%	Merck
Ethanol (absolute for synthesis)	C_2H_6O	> 99.9%	Merck
Nitric acid 65% (for analysis)	HNO_3	65%	Merck
Deionized water	H_2O	18.2 MΩ-cm	
Trimethoxy-methylsilane (MTMS) for synthesis	$C_4H_{12}O_3Si$	> 98%	Merck
Triethoxy-methylsilane (MTES) for synthesis	$C_7H_{18}O_3Si$	> 97%	Merck

Reagent	Chemical Formula	Purity	Provider
Polyvinyl alcohol (PVA) hydrolysis grade	$(C_2H_4O)_n$	98%	Merck
Aluminium-tri-sec-butoxide for synthesis	$C_{12}H_{27}AlO_3$	> 97%	Merck
Potassium bromide (pusriss p.a for IR spectroscopy)	KBr	99.5%	Fluka
Titrant 5 (Titrant for volumetric Karl Fischer titration, contains methanol)	-	-	Merck
Solvent (Solvent for volumetric Karl Fischer titration, contains methanol)	-	-	Merck
Sulfuric acid	H_2SO_4	95-97%	Merck
Ethanol	C_2H_6O	99.5%	J.T. Baker
Methanol	CH_4O	> 99.9%	Merck
1-Butanol	$C_4H_{10}O$	99.5%	J.T. Baker
1-Pentanol	$C_5H_{12}O$	98%	Panreac
Argon	Ar	99.999%	Air Liquide
Hydrogen	H_2	99.999%	Air Liquide
Oxygen	O_2	99.999%	Air Liquide
Mixture ethanol-water-argon	27.6 vol.% C_2H_6O, 3.7vol.% H_2O, 68.7vol.% Ar	99.9%	Own production
Liquid Nitrogen	N_2	-	Praxair

2.2 Synthesis of silica xerogels

In order to study silica (SiO_2) as a useful material in the adsorption of organic compounds (alcohols) as well as in the separation of organic compounds and water, silica xerogels were prepared as powder material and membranes. Below, the preparation of hydrophilic and hydrophobic silica powders and membranes are presented.

2.2.1 Silica powders

2.2.1.1 Hydrophilic silica preparation

Hydrophilic silica xerogels were prepared by acid catalysed (HNO_3) sol-gel method, using the standard TEOS (1) : ethanol (3.8) : water (6.4) : nitric acid (0.085) molar ratio (De Vos et al., 1999; de Lange et al., 1995b; Peters et al., 2005; de Vos & Verweij, 1998). The synthesis was based on the hydrolysis, condensation of tetraethyl-orthosilicate (TEOS) dissolved in ethanol and posterior drying of the wet alcogel at atmospheric pressure. Finally, the obtained gel was cooled and divided in two parts. One part was diluted with ethanol, as previously reported by Peters et al. (2005), and other one was kept as prepared (undiluted). The final density and viscosity of the obtained silica diluted gel was 0.79 $g.cm^{-3}$ and 1.29 cP, respectively (section 2.3.1). After drying, the material was calcined in air, at 400°C.

2.2.1.2 Hydrophobic silica preparation

Hydrophobic silica xerogels were prepared via two different methods: co-precursor (Schwertfeger et al., 1994) and derivatization (Yokogawa & Yokoyama, 1995), using two different hydrophobic agents (trimethoxy-methylsilane, MTMS or triethoxy-methylsilane, MTES).

The co-precursor method was based on the hydrolysis and condensation of TEOS:MTMS or TEOS:MTES mixture dissolved in ethanol, under acidic conditions. Next, drying of the wet alcogel at atmospheric pressure was realized. The derivatization method was based on the hydrolysis and condensation of TEOS dissolved in ethanol under acidic conditions. Next, the chemical modification of the as-synthesized gel using MTMS or MTES was realized. Finally, drying of the wet alcogel at atmospheric pressure was performed. The composition of the reaction mixture (molar ratio to TEOS) was TEOS (1) : ethanol (3.8) : water (6.4) : nitric acid (0.085) : MTMS or MTES (0.5).

2.2.1.2.1 Co-precursor method

Hydrophobic silica xerogels were prepared by acid catalysed (HNO_3) sol-gel method. The synthesis was based on the hydrolysis, condensation of tetraethyl-orthosilicate (TEOS) and hydrophobic agent (MTMS or MTES) dissolved in ethanol and posterior drying of the wet alcogel at atmospheric pressure.

Finally, the obtained gel was cooled and diluted with ethanol in order to obtain a solution viscosity of 1.29 cP, similar to that of the hydrophilic silica gels. After aging and drying at room temperature, the material was calcined in air, at different temperatures. The effect of the calcination temperature on the hydrophobic properties of the synthesized material was also studied.

2.2.1.2.2 Derivatization method

The alcogel derived from TEOS hydrolysis and condensation (prepared using the synthesis procedure presented in section 2.2.1.1) was put in contact with a solution of hydrophobic reagent (MTMS or MTES) and ethanol to obtain the chemical modification of silica surface, as reported by Venkateswara Rao et al. (2004). Subsequently, the gel was washed; during this process unreacted and trapped components on the gel can be removed by immersing the modified silica gel in ethanol (Venkateswara Rao et al., 2004). During the washing process, the presence of two phases was observed, the modified gel and some sedimented particles. Two phases were separated by decantation in order to analyze their origin. Their properties were studied in detail. In the last step of gel preparation, modified silica gel was diluted in ethanol to obtain a solution viscosity of 1.29 cP, similar to that obtained for hydrophilic silica gels after dilution with ethanol. After aging and drying at room temperature, the material was calcined in air, at different temperatures. As above (section 2.2.1.2.1), the effect of the calcination temperature on the hydrophobic properties of the synthesized material was also studied.

2.2.2 Membranes

Hollow fibers ceramic membranes with length of 30 cm and pore size of 200 nm were used as a support. Next, three layers of γ-alumina and three layers of silica xerogel were deposited by dip-coating method over ceramic supports. Figure 2-1 presents their configuration on the outer side of ceramic support.

Figure 2-1. Silica membrane configuration

2.2.2.1 γ-alumina preparation

Boehmite (γ-AlOOH) sol used for the formation of mesoporous γ – alumina layer was synthesized according to the procedure presented by Peters et al. (2005). Aluminium-tri-sec-butoxide ($C_{12}H_{27}AlO_3$) was added to deionized water under vigorous stirring. The water/alkoxide ratio was kept 70:1. After hydrolysis, the boehmite/water mixture was boiled in order to remove the alcohol (2-butanol) produced during the hydrolysis. Subsequently, the obtained slurry was peptized with 1M nitric acid (HNO_3) by refluxing for at 90°C. Boehmite solution was prepared diluting the obtained sol with polyvinyl alcohol (PVA) solution and stirring at room temperature and next at 90°C. The PVA solution was prepared dissolving PVA powder in 0.05M HNO_3. The final solution was stored at room temperature.

2.2.2.2 Silica xerogel solution preparation

Hydrophilic and hydrophobic silica xerogel solutions were prepared for the posterior deposition of silica membranes. Hydrophilic silica gel was prepared by acid catalysed (HNO_3) sol-gel method, using the standard TEOS (1) : ethanol (3.8) : water (6.4) : nitric acid (0.085) molar ratio, as described in section 2.2.1.1. Finally, the resulting solution was diluted with ethanol. Hydrophobic silica gel was prepared by co-precursor method using MTMS as hydrophobic agent, as described in section 2.2.1.2.1. Finally, the resulting solution was diluted with ethanol.

2.2.2.3 γ-alumina and silica layers deposition

The γ-alumina and silica deposition was realized by a dip-coating method, performed at room temperature, in a cupboard to minimize dust contamination. The boehmite solution was deposited at the dip-coating velocity reported by Noriega (2010). Next, the alumina membrane was dried and calcined at 600°C. This procedure was repeated 2 times, to obtain three γ-Alumina layers over the surface of ceramic support.

In the case of silica layers deposition, at first three different dip-coating velocities (0.5, 1.0 and 1.5 $cm.s^{-1}$) were considered, in order to choose the most favorable, considering the membrane performance. For the subsequent studies, the dip-coating velocity of 1.0 $cm.s^{-1}$ was applied. Each deposited silica layer was dried and calcined in air, at different temperatures.

2.3 Characterization methods

Physico-chemical, structural, textural and morphological properties of hydrophilic and hydrophobic silica gels were determined using different techniques: density and viscosity measurements, TGA (Thermogravimetric Analysis), DTA (Differential Thermal Analysis), MS (Mass Spectrometry), FTIR (Fourier Transform Infrared Spectroscopy), SEM-EDS (Scanning Electron Microscopy and X-ray Energy Dispersive Spectroscopy), XRD (X-ray Powder Diffraction), specific surface area and porosity measurements. Moreover, alcohols and water adsorption experiments as well as the pervaporation experiments of ethanol-water mixtures were performed with synthesized materials. Silica xerogels dried and calcined were characterized using those techniques.

2.3.1 Density and viscosity measurements

The dynamic viscosity of silica alcogel diluted in ethanol was determined using a Höppler viscometer (Sheen Instrument, England). This measurement is based on the fact that the viscosity of the studied liquid modifies the speed of a ball falling through it. Therefore, the time at which a ball moves in a glass tube from one place to another was determined. The dynamic viscosity of silica alcogel was calculated according to the equation (22):

$$n = K(\rho_S - \rho_L)t \qquad (22)$$

where:
n: is the dynamic viscosity
K: is the viscometer constant ($2.10085x10^{-3}$ $cm^2.s^{-2}$), determined using viscosity of ethanol
ρ_S: is the density of a ball (2.18685 $g.cm^{-3}$)
ρ_L: is the fluid density
t: is the time at which a ball moves from one place to another

Density was measured using a 5 ml pycnometer (Duran, Germany), calibrated with distilled water at 20°C.

2.3.2 Thermal analysis (TG-DTA-MS)

Thermo-gravimetric analysis (TGA) is the study of the sample mass changes as a function of the increasing temperature, in the controlled atmosphere (Brown, 2001; Speyer, 1994). The mass variation can be related to a loss of mass (desorption, drying or decomposition) or a gain of mass (oxidation reaction). The TGA results can be presented in a wide variety of graphical ways; usually as mass or mass percent loss as a function of temperature or time. Numerical derivative TG trace (DTG) can also be obtained in the analysis. Those data are useful to clearly identify the temperatures at which a maximum mass loss takes place.

Differential thermal analysis (DTA) is the simplest and most widely used thermal analysis technique (Brown, 2001). The differences in the temperature between the sample and the reference material are recorded, while both materials are subjected to the same heating program. The reference material is any substance which undergoes no transformation in the studied temperature range. Alumina (Al_2O_3) and carborundum (SiC) have been extensively used as a reference material for organic samples (Brown, 2001). Endothermic thermal effect (ΔH positive) takes place by dehydration of the sample; in this case, a negative peak is presented in DTA curve. Exothermic effects (ΔH negative) are related to the decomposition of the sample (oxidation reaction) and are evidenced as positive peaks. The area under the endothermic or exothermic peak is related to the value of the enthalpy change (ΔH) for the thermal effect (Brown, 2001).

If the DTA and TGA measurements are coupled with a gas analysis technique, such as a mass spectrometry (MS), the determination of the nature of evolved gaseous reactions products is possible (Brown, 2001; Speyer, 1994).

In this study, the TGA-DTA-MS analysis of silica gel was used to determine its thermal stability and the temperature range of its operation. TGA-DTA-MS analyses were performed on powder materials using a Setsys 16/18 (Setaram, France) TGA-DTA instrument, coupled with a quadrupol mass spectrometer (Balzers Thermostar, Liechtenstein). Data acquisition was performed continuously using a commercial interface and software. The alumina (Al_2O_3) crucible containing approximately 20 mg of sample was heated from room temperature up to 800°C, in air (40 $cm^3.min^{-1}$), with a ramp rate of $1°C.min^{-1}$. Corresponding m/z values 16 (O^+, H_2O), 17 (OH^+, H_2O), 18 (H_2O^+, H_2O), 30 ($C_2H_6^+$, C_2H_6), 31 ($C_2H_2OH^+$,C_2H_3OH), 43 ($C_2H_3O^+$, C_2H_5OH), 44 (CO_2^+, CO_2), 45 ($C_2H_5O^+$, C_2H_5OH) and 46 ($C_2H_5OH^+$, C_2H_5OH) were monitored by mass spectrometry.

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is one of the most common spectroscopic techniques used to determine the chemical functional groups of a solid sample (Griffiths & Haseth, 2007; Sherman Hsu, 1997; Stuart, 2004). When a material is exposed to the infrared radiation, its chemical bonds start to vibrate at a characteristic frequencies and modes, giving a particular adsorption band or peak in the FTIR spectrum. The studies of these bands allow to identify the functional groups and to obtain useful structural information, comparing the absorption bands of a sample to a table of functional group adsorption frequencies.

The majority of FTIR experiments are currently performed in the transmission–absorption mode. Transmittance is traditionally used for spectral interpretation, while absorbance is used for quantitative work (Ryczkowski, 2001; Stuart, 2004). Transmission mode is the simplest sampling technique in FTIR spectroscopy and is used for routine spectral measurements. A small amount of the solid sample is mixed with powdered potassium bromide (KBr), which is completely transparent in the mid-infrared region. The sample and KBr mixture is pressed to obtain a good pellet and yield good spectra (Ryczkowski, 2001).

FTIR characterization of hydrophilic silica xerogels calcined at 400°C was performed in a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, USA) with MCT detector (photoconductive detector HgCdTe) using a standard sample holder. Transmittance measurements were performed using KBr technique. Pellets were prepared with 5wt.% of silica and 95wt.% of potassium bromide (KBr) pressed at 1800 psi for 5 minutes. FTIR spectra were recorded in the mid-infrared range of 4000-400 cm^{-1} at room temperature.

Silica xerogels calcined at different temperatures were studied by FTIR technique in a Spectrum BX FT-IR spectrometer (Perking Elmer, USA) with deuterated triglycine sulfate detector (DTGS). Pellets were prepared using 1wt.% silica and 99wt.% KBr pressed at 1500 psi for 1 minute. The spectra were recorded at room temperature in the range of 4000–400 cm^{-1}.

FTIR in situ measurements were also carried out using a high temperature and high pressure cell unit with automatic temperature controller (Specac, England). Approximately 20 mg of silica powder were pressed at 1800 psi for 10 minutes to obtain a pellet which was placed in the cell unit. The temperature of the cell, with the sample inside, was increased and a FTIR spectrum of the sample in air atmosphere using the Nicolet 6700 FT-IR spectrometer was recorded.

2.3.4 Scanning Electron Microscopy with X-ray energy dispersive spectroscopy (SEM-EDS)

Scanning electron microscopy is one of the most widely-used surface analytical techniques (Egerton, 2005; Leng, 2008). High resolution images of the surface morphology, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 - 30 keV, and generate many low-energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface morphology of the sample. An image of the sample surface can be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. In addition to low energy secondary electrons, backscattered electrons and X-rays are also generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays emitted from the sample can give more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 μm^3.

Morphological studies of silica xerogels were performed using a S-4700 Scanning Electron Microscopy, SEM (Hitachi, Japan) coupled with Energy Dispersive Spectrometer, EDS (Thermo Noran, USA) at an acceleration voltage of 25 kV. SEM images were recorded at several magnifications (500X - 20.000X). The content of elements in the studied microarea of the oxide surface layer was determined by the EDS method basing on the obtained characteristic X-ray spectra. The examined silica samples were placed on carbon plasters in a holder and before analysing were coated with a carbon monolayer using Cressington 208 HR system (Cressington Scientific Instruments Ltd., UK) in order to reduce the charge build-up on the samples.

Hydrophilic silica membranes were cut in a cylindrical shape of 1.5 cm of length in order to be characterized with SEM. They were carried out in the cylinder's cross and lateral section.SEM micrographs of silica and alumina were obtained. The EDS studies were performed in order to identify the silica layer coated on alumina layers.

2.3.5 X-ray diffraction (XRD)

When X-ray radiation passes through the matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. It results in the diffraction in places where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures. Most crystals can have many sets of planes passed through their atoms. Each set of planes has a specific atomic spacing and will give rise to a characteristic angle of diffracted X-rays (Klung & Alexander, 1974; Perego, 1998). Consequently, XRD results are useful to determinate crystalline phases, their evolution from different treatments and also to evaluate the average particle size and the lattice parameters for a given sample.

The analysis of the crystalline structure of silica xerogels was carried out using X-ray diffraction (XRD). Approximately 500 mg of sample, which had been hand ground in an agate mortar, was packed in the sample holder. XRD patterns were obtained at room temperature using a X-ray diffractometer (Panalytical, Netherlands), equipped with X'Celerator andh nickel-filtered CuKα radiation ($\lambda = 1.5406$ Å). The operation voltage and current were 40 kV and 30 mA, respectively. Data were collected in the 2θ range of 5-90°, with a step size of 0.0170 and step time of 10.34 s. Total analysis was performed using HighScore Plus software in order to identify the crystalline phases of studied samples.

2.3.6 Specific surface area and porosity measurements

The nitrogen adsorption at 77 K is a standard and widely used method to determine the specific surface area and pore size distribution of adsorbents. This technique is also applied to determine the materials microporosity (Kruk & Jaroniec, 1999). The Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938) provides a standard procedure to determine the specific surface area of solid samples. In the evaluation of the surface area by the BET method, based on the physisorption isotherm data, it is necessary to construct the BET plot and determine the value of the monolayer capacity (n_m). Subsequently, the specific surface area can be calculated, considering the average area occupied by each molecule in the completed monolayer (Rouquerol, et al., 1999). BET equation is conveniently expressed in the linear form as presented below (equation (23)).

$$\frac{p/p^o}{n(1-p/p^o)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\left(\frac{p}{p^o}\right) \tag{23}$$

where: p : is the working pressure
n : is the amount of gas adsorbed at working pressure
p^o: is the vapor pressure of a gas at adsorption temperature

n_m: is the amount of the adsorbed gas when the entire adsorbent surface is covered with a monolayer
C: is the constant related with the adsorption energy of the adsorbed monolayer

BET plot of $(p/p^o)/n(1-p/p^o)$ versus p/p^o should be a straight line (within the relative pressure ranges p/p_o ~ 0.05 and p/p_o ~ 0.3) with the slope (s) and intercept (i) presented in equations (24) and (25).

$$s = \frac{(C-1)}{n_m C} \tag{24}$$

$$i = \frac{1}{n_m C} \tag{25}$$

The specific surface area, a_{BET} can be calculated basing on the BET monolayer capacity, n_m, applying the simple relation (26):

$$a_{BET} = n_m L \sigma \tag{26}$$

where L is the Avogrado constant and σ is the average area occupied by each molecule in the completed monolayer (for nitrogen (N_2) adsorption at 77 K, the value of σ is 0.162 nm^2).

Brunauer and co-workers have classified physical adsorption isotherms into five characteristic types shown in Figure 2-2. Type I isotherms show a fairly rapid rise in adsorbed quantity with increasing concentration (or pressure) up to saturation. This isotherm is characteristic of microporous adsorbents. The adsorption isotherm Type II indicates a multilayer adsorption. Type II isotherms are obtained with non-porous or macroporous adsorbents, which allow unrestricted monolayer-multilayer adsorption to occur at high concentration. Type III isotherm is convex to the concentration axis over the complete range. This feature is indicative of weak adsorbent-adsorbate interactions. Adsorption isotherm of Type IV is similar as that of Type I. The only difference between the two types of isotherms is that the concavity in the case of Type IV is positive at low concentrations. Adsorption isotherm of mesoporous materials is a good illustration for Type IV isotherm. The adsorption isotherm of Type V is similar to that of Type II except that the behavior at low concentrations. The molecules which are adsorbed at low concentrations present a sort of dimerization (Khalfaoui et al., 2003).

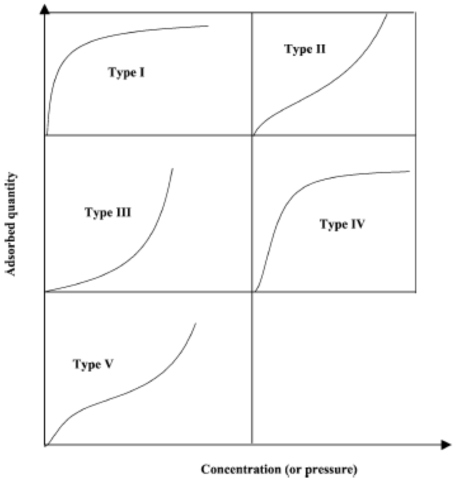


Figure 2-2. The five types of adsorption isotherm, I to V, in the clasification of Brunauer, Emmett, and Teller (Khalfaoui et al., 2003)

Many methods to determine the pore size are currently available. Therefore, it is important to choose an appropriate tool for the analysis (Rouquerol et al., 1999). One of methods used for the determination of pore-size distribution in the micopore range is HK method, proposed by Horvath and Kawazoe (1983). It is based on the general idea that the relative pressure required for the filling of micropores of a concrete size and shape with adsorbate is related to the adsorbent-adsorbate interaction energy (Rouquerol et al., 1999). This means that the micropores are progressively filled with an increase in adsorbate pressure (Roque-Malherbe, 2007). Horvath and Kawazoe equation (27) is base in the adsorption of nitrogen by molecular sieve carbons at 77 K.

$$ln(p/p^{o}) = \frac{61.23}{(H-0.64)}\left[\frac{1.895\times10^{-3}}{(H-0.32)^{3}} - \frac{2.709\times10^{-7}}{(H-0.32)^{9}} - 0.05014\right] \qquad (27)$$

where H is the microporous width in nm (microporous diameter).

In this study, the specific surface area, pore volume, pore size and pore size distribution were measured for hydrophilic and hydrophobic silica xerogels by nitrogen physisorption at liquid nitrogen temperature using a Gemini 2360 (Micromeritics, Germany) surface area analyzer. Prior to the measurement, approximately 0.4 g of silica xerogels were degassed for 480 minutes at 200°C. The specific surface area was calculated according to the BET theory while the pore size distribution and the pore volume were calculated by the Horvath and Kawazoe (HK) method for microporous materials.

2.3.7 Adsorption studies

The change in the concentration of a component in the surface layer of the adsorbent in comparison with the bulk phase is named as adsorption. It involves selective uptake of the adsorbate from the bulk phase onto a phase provided by the adsorbent (Parida et al., 2006). Adsorption is due to the interactions between the solid and the molecules in the fluid phase. Two kinds of forces are involved, which give rise physical adsorption (physisorption) or chemical bonding (chemisorption). Physisorption forces are responsible for the condensation of vapors whereas chemisorption interactions are responsible for the formation of chemical compounds (Rouquerol et al., 1999).

At adsorption of organic compounds on hydroxylated silica surface, two types of main interactions are manifested: van der Waals being universal for any compounds and interactions with formation of hydrogen bonds between the surface silanols groups and adsorbed electron donor molecules. Hydrogen bonding in many cases brings the essential contribution to the adsorption energy and determines the adsorption process (Papirer, 2000).

In this thesis, the adsorption studies of the mixture ethanol-water over silica xerogels were performed. This binary system appears to be very interesting in the field of bio-fuels. However, one of the most important requirements of ethanol to be applied as oxygenate for gasoline, is its required dehydration degree (99.5%). Moreover, the silica xerogels adsorption capacity of pure alcohols such as methanol, ethanol, n-butanol and 1-pentanol was performed. Methanol, ethanol and n-butanol were chosen due to their potential application as alternative fuel to petroleum; whereas 1-pentanol was selected due to its relation with the ethanol production.

The obtaining of adsorption isotherms and the fitting of experimental data to adsorption models are not part of the aim of this thesis. Therefore, adsorption studies were used just to select the silica material which presents the more appropriated hydrophobic character with the criterion of highest ethanol adsorption capacity of ethanol-water mixture in the adsorption studies in liquid and gas phase.

2.3.7.1 Alcohols and water adsorption in liquid phase

The adsorption capacity of hydrophilic and hydrophobic silica xerogels was measured for ethanol, water and ethanol-water mixture (5 wt.% of ethanol, 95wt.% of water). It was also determined for pure alcohols: methanol, ethanol, n-butanol and 1-pentanol. Approximately 0.5 g of silica xerogels were put in contact with 2 g of the adsorbate for 12 hours at room temperature (20°C), to guarantee the adsorption under equilibrium conditions.

Next, to determine the amount of wet gel, silica xerogels were centrifuged at 3000 rpm for 5 minutes in a centrifuged 004 special (Indulab, Colombia) to remove the excess of liquid unadsorbed. Silica wet xerogels were dried in an oven at vacuum pressure of 52 mmHg for 7 hours at 75°C to obtain the amount of the substance adsorbed by mass difference. The minimum contact time require to establish equilibrium conditions and dry complete the gel was obtained experimentally.

In the case of the adsorption of ethanol-water mixture, the concentration of ethanol before and after adsorption was measured by High-Performance Liquid Chromatography (HPLC) using Elite LaChrom HPLC (VWR Hitachi, USA) with a transgenomic ORH-801 column. Sulfuric acid 0.0025 N was employed as mobile phase in the HPLC chromatograph and detector and column temperature were fixed at 35°C and 50°C, respectively.

The amount of adsorbed ethanol was determined using the ethanol and global mass balances in the adsorption system, presented in equations (28) and (29) respectively.

$$m_0 = m_l + m_c * RW \tag{28}$$

$$m_0 * w_E^0 = m_l * w_E^L + m_c * RW * w_E^s \tag{29}$$

Where:
m_0: Amount of initial water-ethanol liquid mixture (g)
m_l: Amount of water-ethanol liquid mixture after adsorption process (g)
m_c: Amount of dried silica xerogels (g)
RW: Amount of liquid mixture adsorbed per gram of dried silica xerogel (g / g silica)
w_E^0: Mass fraction of ethanol in the initial liquid mixture
w_E^L: Mass fraction of ethanol in the liquid mixture after adsorption process
w_E^s: Mass fraction of ethanol adsorbed on silica xerogel

The mass fraction of ethanol (E) and water (w) adsorbed on the solid phase (equation (30) and (31)) is obtained by combination of equations (28) and (29).

$$w_E^s = \frac{(w_E^0 - w_E^L)}{RS * Rw} + w_E^L \tag{30}$$

$$w_w^s = 1 - w_E^s \tag{31}$$

$$RS = \frac{m_c}{m_0} \tag{32}$$

Selectivity to ethanol was used as a criterion to select the silica material with highest degree of hydrophobicity. It was defined as the ratio of the mass fraction of adsorbed compounds and the mass fraction of initial water-ethanol liquid mixture, as is presented in equation (33).

$$\alpha = \frac{w_E^S/(1 - w_E^s)}{w_E^0/(1 - w_E^0)} \tag{33}$$

Moreover, selectivity to water was calculated in the case of hydrophilic silica xerogel to confirm the affinity of these material toward water.

$$\alpha = \frac{w_w^S/(1 - w_w^s)}{w_w^0/(1 - w_w^0)} \tag{34}$$

2.3.8 Pervaporation

Pervaporation is a type of membrane separation process with a wide range of uses such as solvent dehydration; removal of trace volatile organic compounds from aqueous solution (water purification) and separation of organic–organic mixtures as an alternative to distillation (Baker, 2004; Chapman et al., 2008; Smitha et al., 2004). Pervaporation has significant advantages in the separation of azeotropic mixtures, close boiling-point mixtures, for the recovery small quantities of impurities and for the enhancement of equilibrium reactions (Chapman et al., 2008). For these reason, pervaporation is considered to be a promising alternative to conventional energy intensive technologies for being economical, safe and eco-friendly (Smitha, Suhanya, Sridhar, & Ramakrishna, 2004).

In pervaporation a liquid feed is passed over the membrane surface and one component is able to pass preferentially as a vapor through the membrane. Transport through the membrane is induced by the vapor pressure difference between the feed solution and the permeate vapor (Baker, 2004; Chapman et al., 2008). The fraction of the feed that diffuses across the membrane is defined permeate, and the fraction retained in the feed side is called retentate. The permeate is condensed to maintain the vapor concentration at the permeate side low, while the retentate is often recycled to the feed tank to allow further separation and to maintain the feed concentration constant in the storage tank (Baker, 2004).

The performance of silica membranes was evaluated by pervaporation experiments. Hydrophilic silica membranes were tested by pervaporation at 70°C of ethanol-water mixture with feed ethanol concentration of 95wt.%, close to the azeotropic point with ethanol composition of 95.7% wt at 585mmHg and 71.65°C. Hydrophobic silica membrane were studied in ethanol removal (7wt.% of ethanol in water) at 35°C, similar conditions employed in the production of ethanol by fermentation process (Noriega, 2010).

Figure 2-3, presents the diagram of laboratory pervaporation set-up. A stainless steel membrane tubular module has used to introduce the silica membrane. The effective length of the membrane was 27 cm to yield a total effective membrane area of 0.00254 m^2. On the membrane feed side, a recycle stream was applied in connection with the storage vessel.

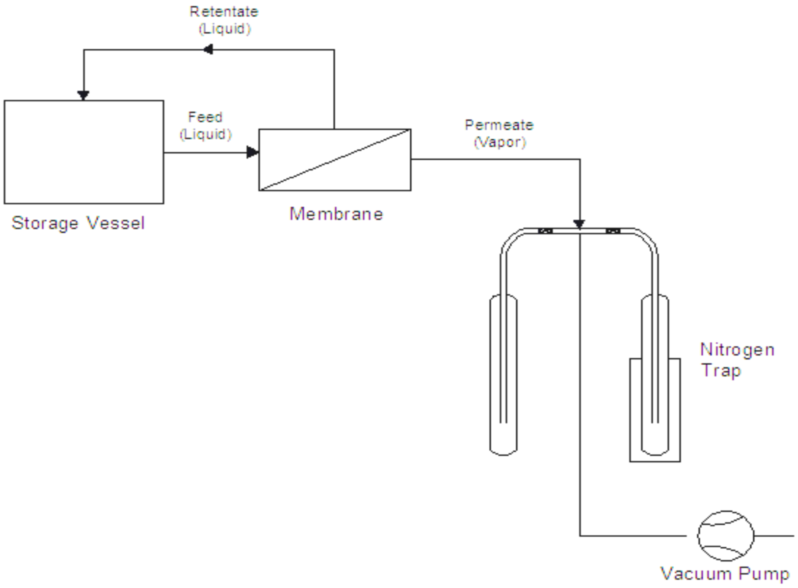


Figure 2-3. Schema of the laboratory pervaporation set-up.

A heating circulator F12 (Julabo, Germany) of 4 liters was used to heat and pump with a flow rate of 16000 ml.min^{-1} the feed liquid from storage vessel to membrane module. On the permeate side vacuum was kept below 3 mbar with a vacuum pump. A liquid nitrogen cold trap was used to collect the permeate for further analysis. For ethanol dehydration, the retentate compositions were analyzed using an automated Karl-Fischer titration apparatus SM 702 titrino (Metrohm, Switzerland), while the permeate compositions were measured by Elite LaChrom HPLC (VWR Hitachi, USA) with a transgenomic ORH-801 column.

Membrane performance was evaluated based on the mass flux across the membrane (J), selectivity (α) and pervaporation separation index (PSI). Permeation flux (J) was calculated from the mass of the permeate collected in a cold trap immersed in liquid nitrogen by unit of time and effective membrane area.

The overall mixture selectivity is defined as the ratio of permeate to retentate compositions, as is showed in equation (35).

$$\alpha = \frac{y_{iP}(1 - x_{iR})}{x_{iR}(1 - y_{iP})} \tag{35}$$

The partial flux of one component through the membrane is a result of total flux multiplied by the mass fraction of the component in the permeate (equation (36)).

$$J_i = J_{total} w_{iP} \tag{36}$$

Pervaporation separation index (PSI), equation (37), which is a relative measure of the separation ability of a membrane, has been defined as the product of the total flux and selectivity (Kaewkannetra et al., 2011; Kanti et al., 2004). Pervaporation separation index (PSI) has been widely accepted to evaluate the overall pervaporation performance of membranes (Nawawi & Hassan, 2003; Sampranpiboon et al., 2000). This value can be used as a relative guideline index to select a membrane with an optimal combination of flux and separation factor.

$$PSI = J_{total} * \alpha \tag{37}$$

Where
α: Selectivity
y_{iP}: Molar fraction of preferential component in permeate side
x_{iR}: Molar fraction preferential component in retentate side
J_i: Mass flux of component i (kg m^{-2} h^{-1})
J_{total}: Total mass flux (kg m^{-2} h^{-1})
w_{iP}: Mass fraction of preferential component in permeate side
PSI: Pervaporation separation index (kg $m^{-2}h^{-1}$)

Chapter 3.
Results and discussion

3.1 Characterization of hydrophilic silica materials

Introduction

This section presents textural, morphological, surface and adsorptive properties of hydrophilic silica xerogels examined using BET, XRD, SEM-EDS, FTIR and adsorption studies. The thermal stability of the synthesized hydrophilic material in air atmosphere was also performed, using TGA-DTA-MS and FTIR techniques. The studied materials were prepared by the sol-gel method under acidic conditions, using the standard TEOS: C_2H_5OH: H_2O: HNO_3 molar ratio of 1:3.8:6.4:0.085. The influence of the aging time at alcoholic conditions on the xerogel properties was investigated. The synthesized silica xerogels were divided in two parts. One part was diluted with ethanol and left to dry at room temperature during 15 days. At these conditions slow evaporation of solvent takes place and the strength of the gel increases. Moreover, it could be considered as its aging process in alcoholic solution. Another part of alcogel (without ethanol extra) was left to dry at room temperature during 5 days. The corresponding codification of the synthesized samples is presented in Table 3-1.

Table 3-1. Codification of hydrophilic silica xerogel prepared under different conditions

Sample	Description
M1	Aging for 15 days
M2	Aging for 5 days

The fields of possible applications of obtained hydrophilic silica xerogels are also proposed. Thus, its performance in the adsorption of alcohols and in the ethanol purification by pervaporation process is discussed.

3.1.1 Thermal stability

The TGA-DTA-MS analysis of hydrophilic, uncalcined silica xerogels was applied to determine their thermal stability and the temperature range of their application. Those studies were performed in air atmosphere (oxidative). Figure 3-1 presents the thermogravimetric analysis (TGA) curves of hydrophilic silica xerogels, synthesized under different conditions (Table 3-1), realized in a stream of air. Table 3-2 resumes the obtained results.

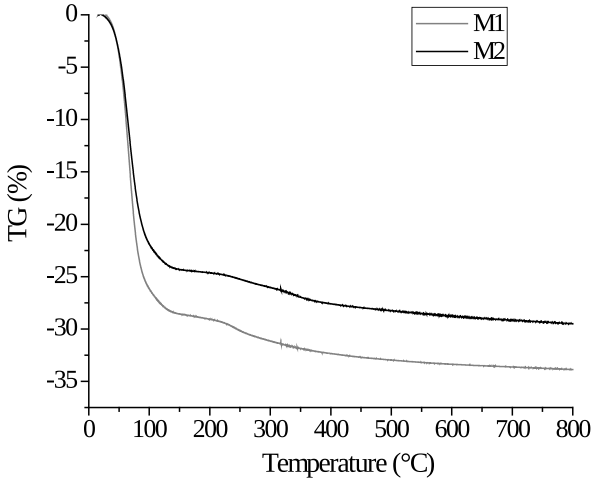


Figure 3-1. TGA curves of hydrophilic silica xerogels in air atmosphere

Table 3-2. The weight loss regions of hydrophilic silica xerogels in air atmosphere

Sample	**% Weight loss**			
	15-150°C	**150-400°C**	**> 400°C**	**Total**
M1	29	4	1	34
M2	24,5	3	1,5	29

In order to explain the performance of the hydrophilic silica xerogels under increasing temperature, the differential thermal analysis (DTA) and mass spectrometry (MS) studies were also performed. The representative TGA-DTA curves obtained for one of the studied samples (M1), in air atmosphere, are presented in Figure 3-2. Table 3-3 summarizes corresponding response of MS coupled with TGA-DTA analysis. Similar results were also obtained for the other studied samples of hydrophilic silica xerogels.

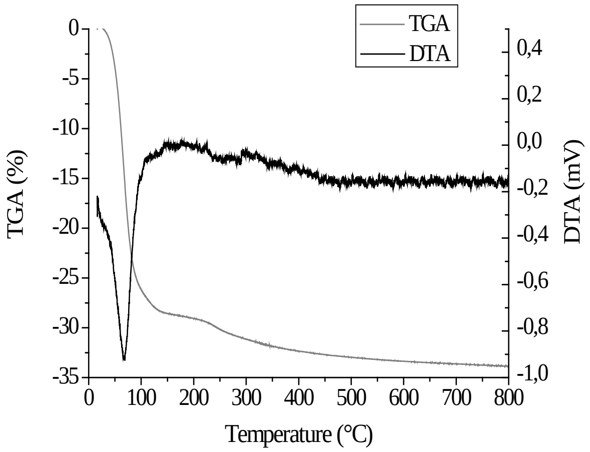


Figure 3-2. TGA-DTA studies of hydrophilic silica xerogel (sample M1) in air atmosphere

Table 3-3. The summary of MS results for hydrophilic silica xerogel (sample M1) in air atmosphere

Mass number (m/z)	Temperature (max. intensity) (°C)	Temperature range (°C)	Intensity ion current (A)	Key fragments	Probable parent molecule
17	50	15-150	1,86 x10^{-11}	OH^+	H_2O
18	50	15-150	8,64 x10^{-11}	H_2O^+	H_2O
18	230	170-320	3,50 x10^{-10}	H_2O^+	H_2O
44	77	50-150	2,70 x10^{-12}	$C_2H_4OH^+$	C_2H_5OH
44	275	200-350	2,62x10^{-12}	CO_2^+	CO_2
46	90	40-130	2,15 x10^{-13}	NO_2^+	NO_2

Independent of the synthesis conditions, the TGA thermograms of hydrophilic silica xerogels (Figure 3-1) obtained in air exhibit three main regions of weight loss. Through the first weight loss region of ca. 28%, in the temperature range 15-150°C, desorption of physically adsorbed and/or trapped in the xerogel network water and ethanol occurs, as confirmed by MS studies (Table 3-3). In this temperature range, the presence of an endothermic peak in the DTA curve (Figure 3-2), with the maximum at ca. 65°C, was also observed, confirming the desorption of physisorbed water and ethanol. Moreover, the decomposition of the residual nitric acid, used as a catalyst during the xerogel synthesis, with a maximum at ca. 90°C, is observed (Table 3-3). The second weight loss region of ca. 4%, in the temperature range 150-400°C, could be assigned to the removal of residual organic compounds and further polymerization of the silica network. The presence of H_2O^+ (m/z=18) and CO_2^+ (m/z=44) species in the MS spectrum in this temperature range was also observed (Table 3-3), suggesting residual TEOS decomposition. It should be noted that the boiling point of TEOS (ca. 170°C) agrees with the observed effects. The obtained results are in agreement with those reported by Van Der Vis et al.(1993), which suggested that H_2O and CO_2 are products of TEOS decomposition in the presence of oxygen. At 400°C, the total weight loss of hydrophilic silica xerogels is about 32%. The further weight loss of ca. 2%, at temperature above 400°C, is related with the removal of OH-groups from de silica surface, as previously reported by Brinker & Scherer (1990). Therefore, the temperature of 400°C can be proposed as the minimum calcination temperature for hydrophilic silica xerogels. It should be also noted that the aging of the synthesized alcogel in the alcoholic solution does not influence the thermal stability of the studied xerogels (Figure 3-1).

In order to confirm the phenomena observed during the thermal treatment of hydrophilic silica xerogels in air atmosphere, in situ FTIR studies with the programmed increase in the temperature were also performed. Figure 3-3 depicts the representative FTIR spectra of one of studied samples (uncalcined sample M1,Table 3-1) recorded in the temperature range 20-400°C, in air atmosphere. The identified bands in the silica spectra are summarized in Table 3-4.

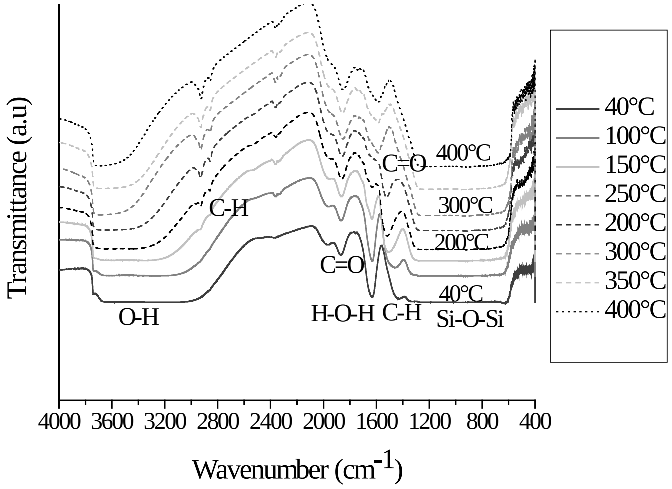


Figure 3-3.The influence of the temperature on the FTIR spectra of hydrophilic silica xelogel (uncalcined sample M1)

Table 3-4. Characteristic vibration frequencies in FTIR spectra of hydrophilic silica xerogel realized under increasing temperature (uncalcined sample M1)

Wavenumber (cm^{-1})	**Vibration type**	**Structural unit**	**Reference**
3740	Si-OH	Si-OH…H_2O	(Takei, 1999)
3664-2966	O-H	H-O-H…H_2O	(Al-Oweini & El-Rassy, 2009)
2927	ν_{as} C-H	CH_2	(Al-Oweini & El-Rassy, 2009)
2856	ν_s C-H	CH_2	(Al-Oweini & El-Rassy, 2009)
2364	C=O	CO_2	(Socrates, 1994)
1860	C=O	Carbonyl Groups	(Socrates, 1994)
1640	δ H-O-H	H_2O	(Al-Oweini & El-Rassy, 2009)
1588	C=O	Carbonyl Groups	(Socrates, 1994; Stuart, 2004)
1526	C-H	Si-C_2H_5	(Socrates, 1994)
1270-690	ν_{as} Si-O-Si	Si-O-Si	(Al-Oweini & El-Rassy, 2009; Socrates, 1994)

δ: Deformation vibration, δ_{as}: Antisymmetric deformation vibration, δ_s: Symmetric deformation vibration, ν: Stretching vibration, ν_{as}: Antisymmetric stretching vibration,ν_s: Symmetric stretching vibration,ν_β: In-plane stretching vibration.

The FTIR spectra of the studied hydrophilic silica xerogel show a characteristic broad band in the range of 3664-2966 cm^{-1} assigned to the O-H and SiO-H stretching bands of hydrogen-bonded water molecules and silanols groups on silica surface. The significant reduction in the width of this band under increasing temperature was observed. This effect could be provoked by the water condensation reaction, which reduces the amount of hydroxyl groups, species responsible for water adsorption on silica surface.

At 1640 cm^{-1}, an intense band associated with water adsorption on the surface of the sample is observed. Its intensity significantly decreases with an increasing temperature up to 250°C. Above this temperature this band disappears. Moreover, the reduction in band intensity observed at 1526 cm^{-1}, related to the C-H interaction, in the temperature range 20-250°C was also observed. Those results confirm that in this temperature range the release of ethanol as well as water adsorbed on silica surface occurs.

TEOS thermal decomposition in air atmosphere was evidenced in FTIR experiments at temperatures higher than 250°C. The presence of a new band at 1588 cm^{-1} and the stronger intensity of band at 1860 cm^{-1}, both assigned to C=O interaction of carbonyl groups, are related to the release of CO_2, ethanal and methanol, products of TEOS thermal decomposition at higher temperatures. Moreover, the presence of the broad band in the fingerprint range of 1270-690 cm^{-1} related to the silicon–oxygen covalent bonds vibrations confirms the existence of a dense silica network own of silica xerogels.

Therefore, basing on the TG-DTA-MS and in situ FTIR studies it could be concluded that the release of physically adsorbed and/or trapped in the xerogel network water and ethanol occurs up to 250°C and that the decomposition of silica precursor (TEOS) occurs at higher temperatures. The hydrophilic silica xerogels reached the thermal stability at 400°C in air atmosphere.

3.1.2 Surface characterization

Silica surface characterization was performed by FTIR spectroscopy. The representative FTIR spectrum obtained for one of the studied samples (M1) is presented in Figure 3-4. A complete list of the vibration frequencies and their assignments for FTIR spectra are presented in Table 3-5.

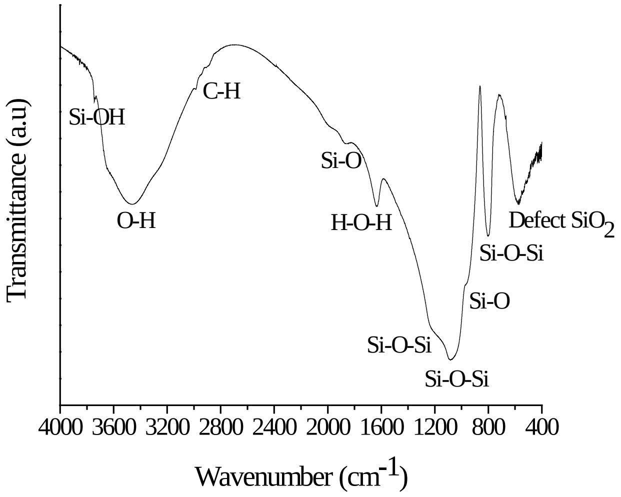


Figure 3-4. FTIR spectra of hydrophilic silica xerogel (sample M1)

Table 3-5. Characteristic vibration frequencies in FTIR spectra of hydrophilic silica xerogel (sample M1)

Wavenumber (cm^{-1})	**Band assigment**	**Structural unit**	**Reference**
3748	Si-OH	Si-OH	(Takei, 1999)
3473	H-O, SiO-H	H-O-H…H_2O and SiO-H…H_2O	(Al-Oweini & El-Rassy, 2009)
2988	ν_s C-H	$-CH_3$	(Al-Oweini & El-Rassy, 2009)
2940	ν_{as} C-H	$-CH_2$	(Al-Oweini & El-Rassy, 2009)
1883	ν_β Si-O	Si-OH	(Lucousky & Pollard, 1983)
1635	δ H-O-H	H-O-H	(Al-Oweini & El-Rassy, 2009)
1381	δ_s C-H	$-CH_2$	(Al-Oweini & El-Rassy, 2009)
1231	δ_s C-H	$Si-C_2H_5$	(Socrates, 1994)
1076	ν_{as} Si-O-Si	Si-O-Si	(Araujo-Andrade & Martínez, 2000)
968	ν_β Si-O	Si-OH	(Al-Oweini & El-Rassy, 2009)
801	ν_s Si-O	Si-O-Si	(Al-Oweini & El-Rassy, 2009)
674	ν_s Si-O-Si	Si-O-Si	(Al-Oweini & El-Rassy, 2009)
576	ν Si-O	SiO_2 Defects	(Al-Oweini & El-Rassy, 2009)

δ: Deformation vibration, δ_{as}: Antisymmetric deformation vibration, δ_s: Symmetric deformation vibration, ν: Stretching vibration, ν_{as}: Antisymmetric stretching vibration,ν_s: Symmetric stretching vibration,ν_β: In-plane stretching vibration.

The FTIR spectrum of the studied hydrophilic silica xerogel shows a characteristic bands at 3748 and 3473 cm^{-1} assigned to the interactions between hydroxyl groups on silica surface and water presented in the surrounding atmosphere. These characteristic bands can be related to the presence of isolated groups (Si-OH) and O-H stretching bands, caused by hydrogen-bonded water molecules (H-O-H …H) and surface silanol groups, hydrogen-bonded to the molecular water (SiO-H…H_2O). The other characteristic bands which confirm the hydrophilic character of silica are located at 968 cm^{-1} and 1883 cm^{-1}, and are directly related to the Si-O interaction of silanol groups.

At 1640 cm^{-1}, an intense band associated with water adsorption on the surface of the sample is also observed due to its hydrophilic nature. The other bands in the range of 1200-1000 cm^{-1} and at 800 cm^{-1} also appeared. These interactions can be related to the antisymmetric and symmetric vibration between Si-O-Si with the minimum at 1076 cm^{-1} and 801 cm^{-1}, respectively. The vibration mode appearing at 1231 cm^{-1} can be assigned to the symmetric deformation of C-H in CH_2 groups, corresponding to residual non-hydrolyzed alkoxy groups ($-OC_2H_5$) on the silica xerogel.

The influence of different parameters such as aging time as well as calcination process on the characteristics of synthesized silica surface was also determined.

Figure 3-5 presents the FTIR spectra of silica xerogels obtained after aging of the corresponding alcogel in alcoholic solution during different periods of time (sample M1 and M2). For both samples, a great similarity in the band frequencies as well as in their intensities is observed. Therefore, no influence of the aging time on the characteristics of the silica surface can be seen.

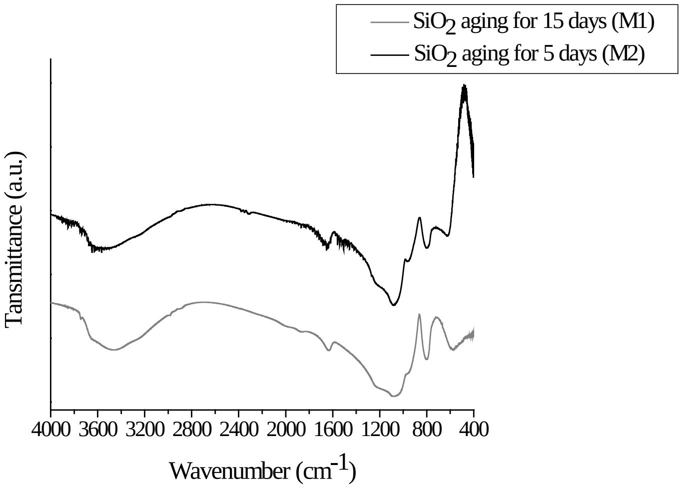


Figure 3-5. FTIR spectra of hydrophilic silica xerogels obtained after aging of alcogel during different periods of time: 15 and 5 days (sample M1 and M2)

Figure 3-6 presents the effect of calcination process on the FTIR spectra of one of the studied silica xerogels (sample M1). The corresponding FTIR spectra were recorded for silica xerogel dried and calcined.

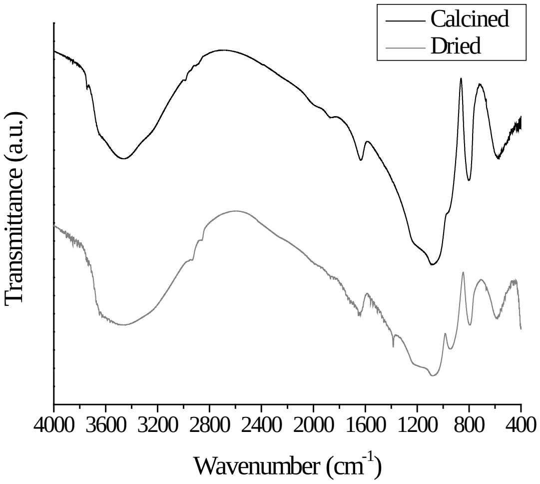


Figure 3-6. Effect of calcination process on the FTIR spectra of hydrophilic silica xerogel (sample M1)

One can see that only for the sample dried, the characteristic interaction band at 1381 cm^{-1}, which can be related to the C-H interaction of ethyl radicals on silica surface, was observed. These radicals can be formed as a product of condensation reactions between $Si(OH)_4$ and $Si(OC_2H_5)_4$. On the other hand, in the case of the sample calcined, the absence of well defined band at 964 cm^{-1} related to the Si-O interactions was registered. It suggests that during calcination process reduction in the number of silanol groups takes place. This process is accompanied with the formation of a dense silica network by Si-O-Si bonds.

3.1.3 Textural and morphological properties

Textural and morphological properties of the hydrophilic silica xerogels were studied by SEM-EDS, N_2 physisorption and XRD techniques. The influence of different parameters such as the initial hydrolysis temperature, aging time as well as calcination process on the textural and morphological properties of synthesized silica was determined.

The effect of the calcination process on the morphology of the hydrophilic silica xerogels was verified. Some representative SEM micrographs, obtained for one of the studied samples (M1), dried and calcined, are presented in Figure 3-7. A smooth surface without imperfections is noted for dried silica; meanwhile, calcined silica presents a rough surface with notable superficial defects (as marked in the corresponding micrograph, Figure 3-7). The observed imperfections can be formed as a result of removal of water, ethanol and residual organic compounds, encapsulated in silica network, during the heat treatment.

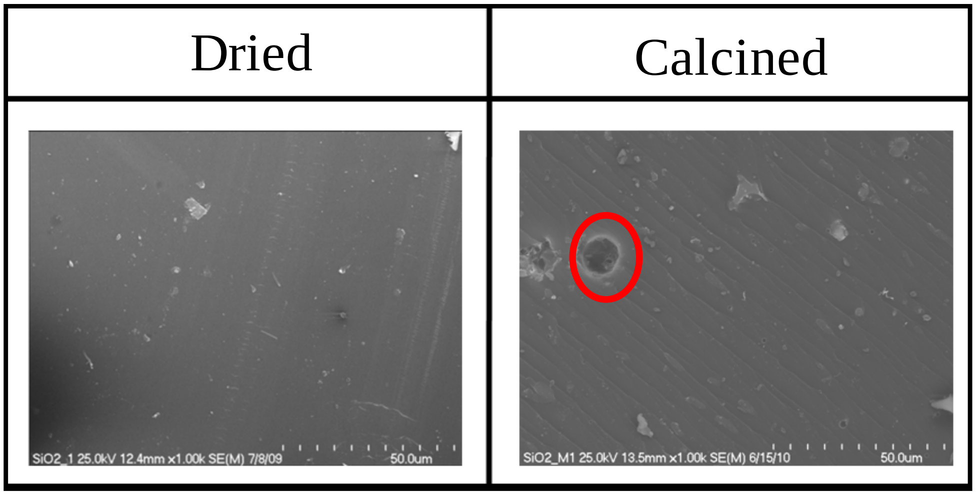


Figure 3-7. SEM micrographs of hydrophilic silica xerogel (sample M1) dried and calcined. Magnification x 1000

Figure 3-8 presents SEM micrographs of hydrophilic silica xerogels, synthesized under different conditions (samples M1 and M2) and calcined. Independent of the synthesis procedure, notable superficial defects (as marked in the corresponding micrographs), in the size of 1-1.2 µm, were found. As suggested above, the observed imperfections can be formed as a result of removal of water, ethanol and residual organic compounds, encapsulated in silica network, during the heat treatment. Moreover, the presence of specific mounds on silica surface was observed. They can be formed as a result of the silica particles agglomeration on the surface.

The significant effect of aging time in alcoholic solution on the morphology of the synthesized xerogeles was observed (Figure 3-8). One can see that longer aging time (15 days) causes the formation of silica characterized with a rough surface (samples M1), while the sample aged only during 5 days present a smoother surface (samples M2). The observed differences in the silica morphology can be attributed to the diverse processes which occur during the alcogel aging. While the aging time increases, the strength of silica xerogel increases due to hydrolysis and condensation reactions that take place during this period of time. Therefore, it is possible that more compact, ramified and rough silica network will be obtained. It should be also noted that higher amount of mounds are presented on the surface of the silica gels aged during 15 days, comparing to that aged during 5 days. Basing on the EDS studies it was confirmed that the observed mounds correspond to the silica particles, products of possible gel re-precipitacion during long periods of aging.

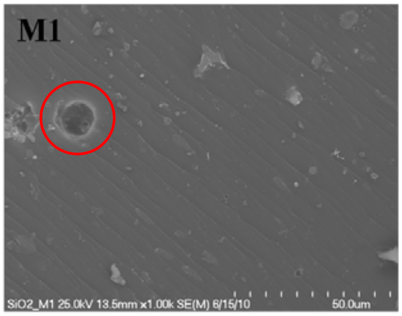
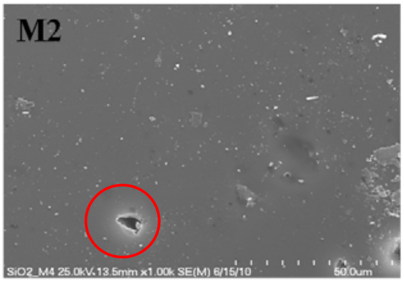
Silica xerogel calcined	
Aged for 15 days	
Aged for 5 days	

Figure 3-8. SEM micrographs of hydrophilic silica xerogels synthesized under different conditions (samples M1 – M2) and calcined. Magnification x 1000

The N_2-physisorption studies over hydrophilic silica xerogels were applied to determine their textural properties. Figure 3-9(a) presents N_2-adsorption isotherms obtained at 77 K for hydrophilic silica xerogels, synthesized under different conditions (M1 to M4) and dried at 40°C. The shape of the isotherms is typically type I, which is characteristic for microporous material (Khalfaoui et al., 2003). One can see that silica xerogels aged during 15 days (M1 and M2) present slightly higher pore volume and adsorb slightly higher amount of gas, comparing to those aged during 5 days. It could be related to more efficient strengthening of silica network during longer aging. Consequently, the formation of stronger silica network probably lets to avoid the drastic reduction of pore volume during drying process.

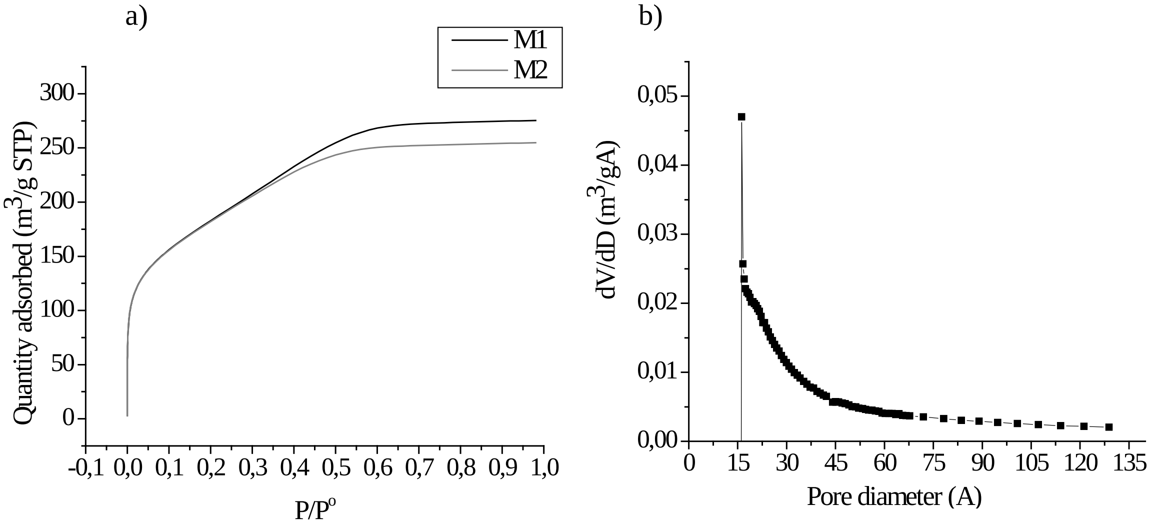


Figure 3-9. N_2-adsorption results: a) Adsorption isotherms at 77K for hydrophilic silica xerogels, synthesized under different conditions (M1 and M42) and dried; b) Pore size distribution calculated using Horvath-Kawazoe model (sample M1)

The representative micropore size distribution, calculated by the Horvath-Kawazoe method (Horvath & Kawazoe, 1983 b), obtained for one of the studied sample (M1), is presented in Figure 3-10 (b). The HK analysis indicates that silica xerogels presents a narrow pore size distribution, with a miximum at 18Å, which correspond to microporous material (D pore < 20Å). Therefore, it confirms that the synthesis of silica xerogels at pH lower than silica isoelectric point (pH≈ 2) leads to formation of small pores size (Brinker & Scherer, 1990). Pore volume, pore width, porosity and specific surface area of the studied samples are reported in Table 3-6.

Table 3-6. Specific surface area, pore volume, porosity and pore width calculated by Horvath-Kawazoe method for hydrophilic silica xerogels, synthesized under different conditions (M1 and M2)

Sample	**Pore width (Å)**	**Pore volume (cm^3/g)**	**Specific surface area (m^2/g)**	**Porosity (%)**
M1	18	0,3220	639	41,5
M2	18	0,3195	631	41,3

The silica samples presents an average pore diameter of 18 Å, micropore volume of ca.0,32 cm^3.g^{-1} and a porosity of 41%. The specific surface area obtained for all materials is very similar ca. 630 m^2.g$^{-1.}$ Concluding, the alcogel alcoholic aging has not influence on the textural properties of hydrophilic silica xerogel.

The calcination process clearly influences the textural properties of the studied samples (Table 3-7). The comparison of the N_2-adsorption isotherms for silica xereogel (sample M1) dried and calcined is presented in Figure 3- 10. Both isotherms are type I, characteristic for microporous materials. As a result of the calcination process, the decrease in the amount of the adsorbed gas takes place, which is strongly related to the pore volume. The calcination of hydrophilic silica xerogel produces the reduction of micropore surface and volume. It should be noted that condensation reactions still continue during calcination process and promote densification of the silica network (Venkateswara Rao et al., 1999). Under increasing temperature, the decrease in the pore volume and specific surface of 17% and 19% respectively, was observed. It was accompanied with the decrease in the sample porosity of ca. 5%, as a result of sample densification.

Table 3-7. Specific surface area, pore volume, porosity and pore width calculated by Horvath-Kawazoe method for hydrophilic silica xerogels (sample M1), dried and calcined

Sample	**Pore width (Å)**	**Pore volume (cm^3/g)**	**Specific surface area (m^2/g)**	**Porosity (%)**
dried	18	0,322	639	41,5
calcined	17	0,2686	518	37,1

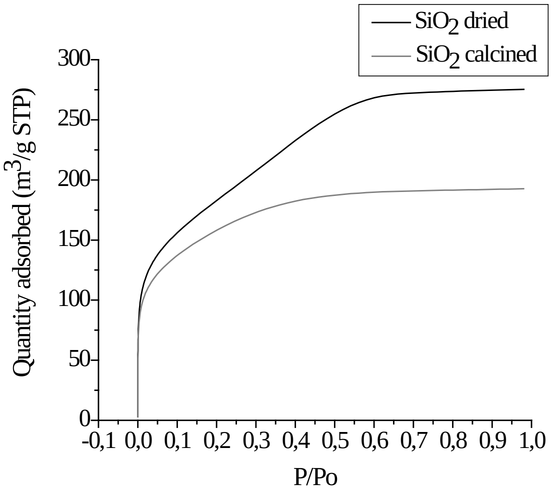


Figure 3- 10. N_2-adsorption isotherms at 77K for hydrophilic silica xerogels (sample M1) dried and calcined

Basing on the X-ray diffraction studies (Figure 3-11), the amorphous character of the studied hydrophilic silica xerogels was confirmed. The XRD pattern presents only broad humps in the range of 2θ: 15-30° as also reported by Czarnobaj (2008).

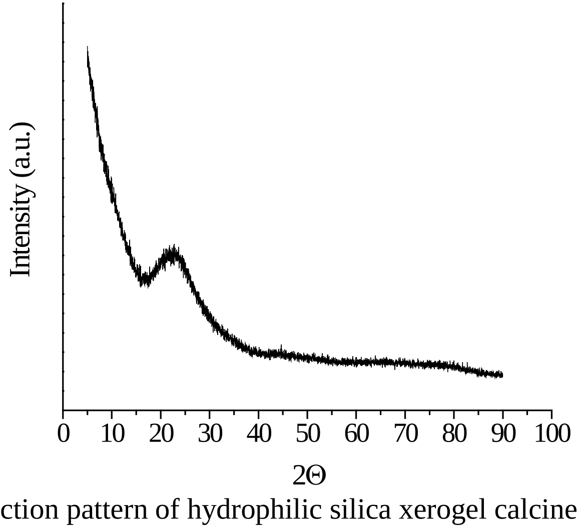


Figure 3-11. X-ray diffraction pattern of hydrophilic silica xerogel calcined at 400°C (sample M1)

3.1.4 Adsorptive properties

The adsorption studies over hydrophilic silica xerogels were performed in liquid phases, over one of the hydrophilic silica xerogels (sample M1), considered as a representative one.

The adsorption studies of pure water, pure ethanol and their mixture (5wt.% H_2O, 95wt.%C_2H_5OH) in the liquid phase were performed over hydrophilic silica xerogels. The concentration of the mixture was selected in accordance to the ethanol dehydration concentration by pervaporation (5-10wt.% H_2O), a potential application of hydrophilic silica material. Figure 3- 12(a) presents the adsorption capacity of silica xerogel (sample M1). One can see that both pure water and pure ethanol were adsorbed on silica surface. Nevertheless, high selectivity towards water adsorption was observed in the adsorption experiment performed with a mixture of 95 wt.% ethanol in water (Figure 3- 12(b)). Selectivity toward water and ethanol were 7,25 and 0,14 respectively.

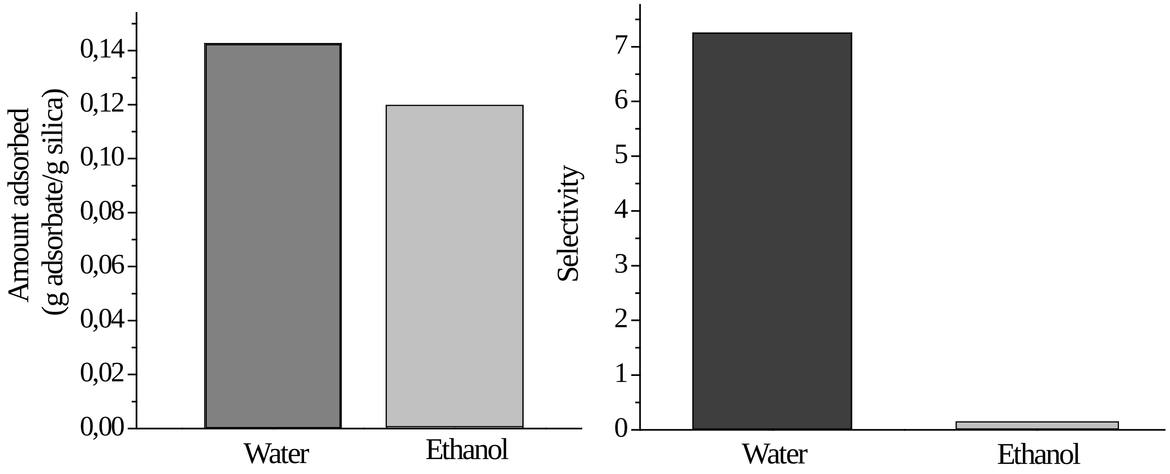


Figure 3- 12. (a) The adsorption capacity of silica xerogel (sample M1), (b) Selectivity toward ethanol and water in the adsorption experiment performed with a mixture of 95 wt.% ethanol in water

According to the literature (Bolis et al.,1997; Holysz, 1998; Turov, 1998), the silanol groups and siloxane bridges are considered as strong adsorption sites on the silica surface, due to the possibility of their interactions with adsorbate molecules by hydrogen bonding. Silanol species can be classified in three groups: isolated, vicinal and geminal (Jal et al., 2004).

The adsorption of water and alcohols can occur via one or two hydrogen-bonding interactions with isolated and vicinal silanol groups, respectively. Figure 3-13 shows the possible schema of ethanol and water adsorption on silica surface. Therefore, the hydrophilic nature of silica gel (presence of Si-OH groups) makes possible the adsorption of ethanol and water molecules on its surface.

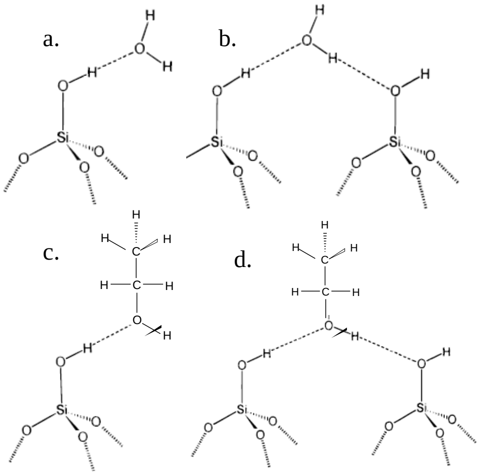


Figure 3-13. Hydrogen-bonding of water and ethanol adsorption: a) water adsorption through isolated silanol group, b) water adsorption through vicinal silanol group, c) ethanol adsorption through isolated silanol group, d) ethanol adsorption through vicinal silanol group (Bolis et al., 1997)

3.1.5 Potential applications

3.1.5.1 Adsorption of alcohols

Silica xerogel can be considered as a good adsorbent material due to their unusual properties, uniform and narrow pore size distribution, small pore size and large specific surface area (Standeker et al., 2007). Figure 3- 14 shows the alcohols adsorption capacity of hydrophilic silica xerogel (sample M1). One can see that pentanol and butanol are adsorbed in slightly higher amounts on silica surface due to their higher molecular height in comparison with methanol and ethanol. This is in agreement with Traube’s rule. It has generally found that adsorption increase with an increase in the molecular weight of the hydrophobic portion of the adsorbate molecule. The longer the hydrocarbon chain in a given series, the largest the amount of substance adsorbed (Myers, 2006). Nevertheless, it is expected that the chemical modification of silica xerogel it will be possible to increase the amount of adsorbed alcohol on its surface. Therefore, it is confirmed that alcohols such as methanol, ethanol, butanol and pentanol can be adsorbed on hydrophilic silica surface by hydrogen bonds due to their hydrophilic nature.

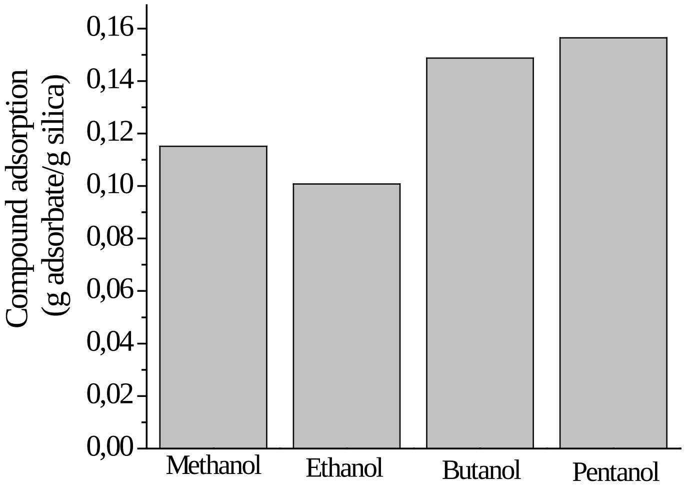


Figure 3- 14. Alcohols adsorption on hydrophilic silica xerogel

3.1.5.2 Silica Membranes

Microporous ceramic membranes offer potential applications in alcohol dehydrations where are needed thermal, mechanic and chemically stable membranes for water-alcohol separations. In the last few years ethanol dehydrations have been received much attention due to the application of anhydrous ethanol as a gasoline oxygenating. Ethanol and water form an azeotrope, at approximately 5 wt.% water content, limiting their complete separation. Traditionally high purity ethanol (99.5%) is obtained by distillation using additional chemicals such as cyclohexane to overcome the azeotropic composition or by adsorption process using molecular sieves (Posada & Cardona, 2010). Thus, pervaporation is an alternative method for alcohol dehydration to break the azeotope without the addition of chemicals (Chapman et al., 2008) and hydrophilic silica membranes have been used for this purpose in pervaporation tests (Ma et al.,2009; Verkerk, 2001).

In this research the performance of silica membranes in ethanol dehydration (5-6 wt.% of H_2O in ethanol) by pervaporation process is studied. The effect of dip-coating velocity and calcination temperature during membrane preparation on membranes flux and selectivity was analyzed.

3.1.5.2.1 Membranes characterization

A typical cross section of a γ-alumina membrane is shown in SEM micrograph in Figure 3-15 (a). The membrane was prepared by three dipping procedures. The thickness of γ-alumina membrane is around 4 µm. It was estimated using the MeasureIT software (Figure 3-16). It can be see clearly that the γ-alumina layer decreases the support roughness, providing to the formation of a smooth surface, ready to deposit silica on the top of it.

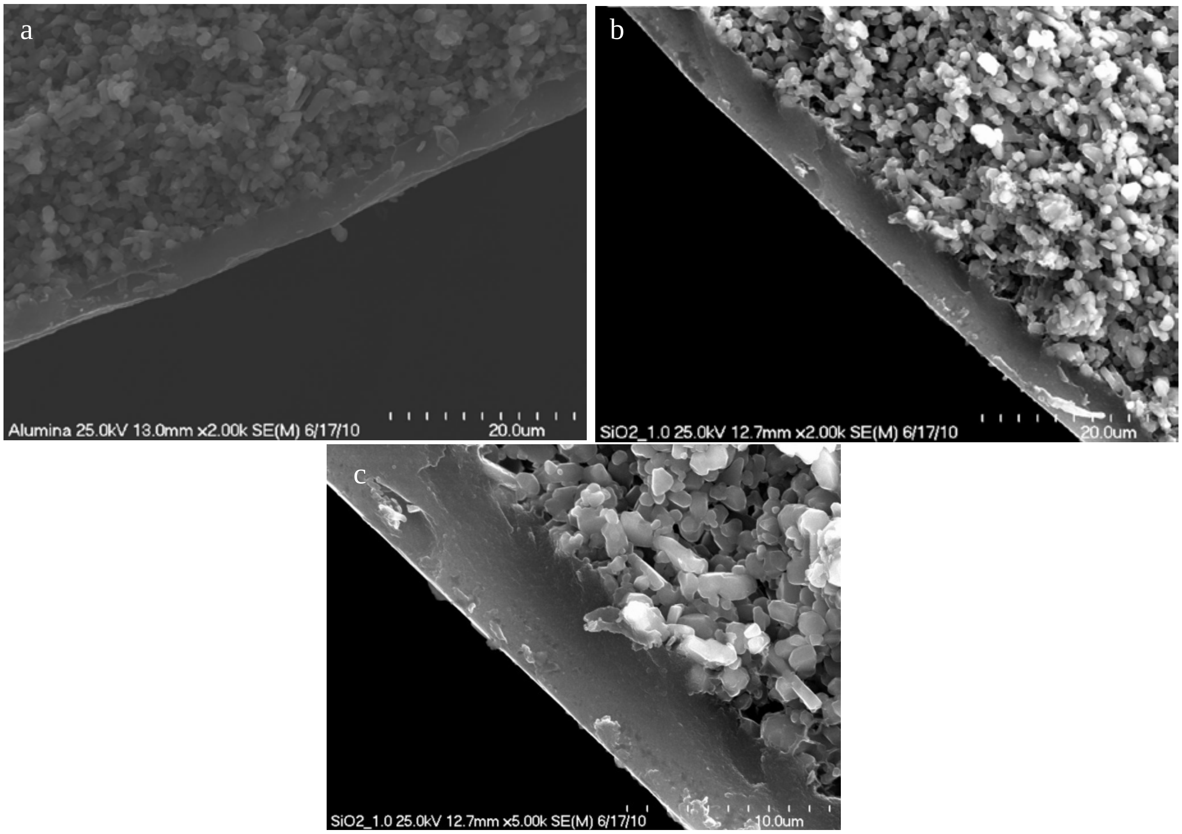


Figure 3-15. SEM micrographs of: a) γ-alumina layers, b) and c) hydrophilic silica membranes deposited with dip-coating velocity of 1cm.s^{-1}. Magnifications x 2000 and x 5000

Figure 3-15 (b) and (c) shows SEM micrographs of silica membranes obtained at magnification x2000 and x5000, respectively. One can see three different morphologies in the membrane's cross section. The first, rough morphology is attributed to ceramic support which provides mechanical stability to silica membrane. The second, the smooth one, is assigned to γ-alumina layer deposited on the top of ceramic support. The last morphology, observed as a bright line in the outer size, is associated with silica layers deposited over the γ-alumina membrane.

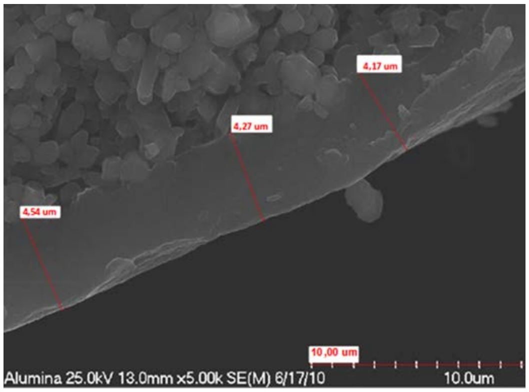


Figure 3-16. SEM micrograph of γ-alumina membrane used to estimate the thickness of γ-alumina layer

The presence of silica on the γ-alumina surface was confirmed by X-ray energy dispersive spectroscopy (EDS) studies. The obtained spectrum for the cross section of silica membrane is presented in Figure 3-17.

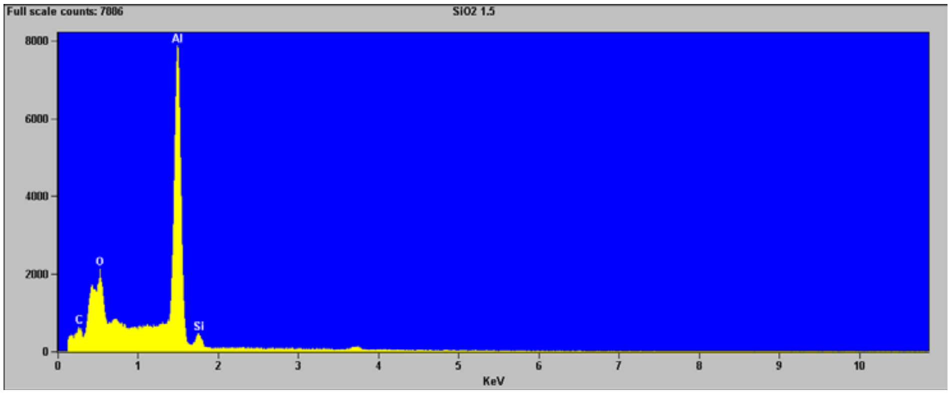


Figure 3-17. EDS spectrum for the cross section of silica membrane (dip-coating velocity of 1cm.s^{-1}).

The corresponding EDS spectrum shows that membrane sample contains Al, Si, O and C. The high content of aluminum (Al) on the membrane's cross section is attributed to the appreciable thickness of γ- Al_2O_3 layer (4 µm) presented on the membrane. One can see the less intensity of silicon (Si) in EDS spectrum. It is attributed to thin thickness of silica layer which difficult the silicon detection. The presence of oxygen (O) and carbon (C) are attributed to aluminum and silicon oxides presented in the membrane and the coating with a carbon layer, respectively.

EDS maps of silica membrane's lateral section was also performed. Figure 3-18 shows the SEM micrograph of a defect on the top of silica layer observed at magnification x1000 and their corresponding EDS maps. This defect could be provoked during the membrane cutting or its storage and transport. The EDS maps of elements present the membrane defects (Figure 3-18 (b-e)) and confirms the presence of silica on the top of γ-alumina layers. The γ-alumina layer was identified as a bright yellow region observed inside the defect (marked in Figure 3-18e). Silica layer were detected as a blue region on EDS map associated to silicon presented on the superior layer of the membrane (marked in Figure 3-18d). The intensity of the studied substances (Al and Si) are different, aluminum presents a measurement scale of 37 to 116 units, while silica presents a lower scale of 0 to 21 units, confirming the low content of silica in the membrane associate with very thin silica layer on the surface of γ-alumina.

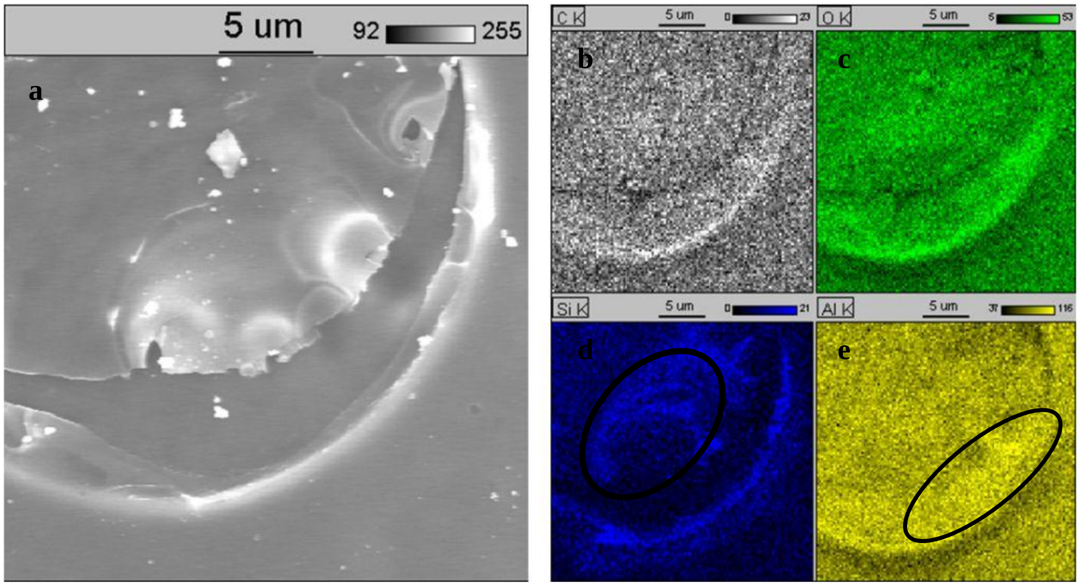


Figure 3-18. EDS maps of silica membrane

The quantification of silica layer thickness was not possible to perform by SEM-EDS technique, due to the lower intensity of silicon on EDS spectra and the difficulty to establish clearly the limit between γ-alumina and silica layer, as it could be seen in SEM micrograph presented in Figure 3-19.

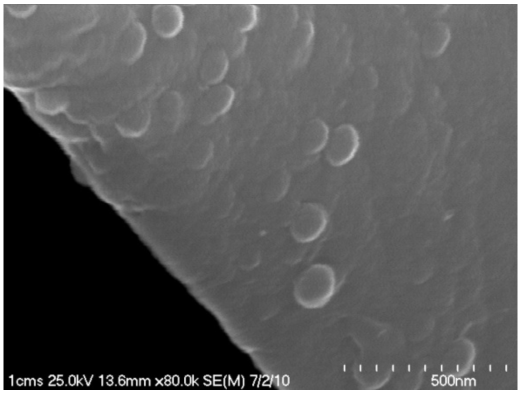


Figure 3-19. SEM micrograph of silica membrane cross section at magnification x 80000

3.1.5.2.2 Ethanol dehydration

Ethanol dehydration studies were performed in order to determine the pervaporation performance of silica membranes. They were deposited with dip-coating velocity of 0.5, 1 and 1.5 cm.s^{-1}. With the aim to select the more appropriated velocity of silica-membrane deposition. Therefore, hydrophilic silica membranes were tested in ethanol dehydration (5wt.% water) by pervaporation at 70°C .The performance of those membranes in the terms of flux, selectivity and PSI are presented in Figure 3-20.

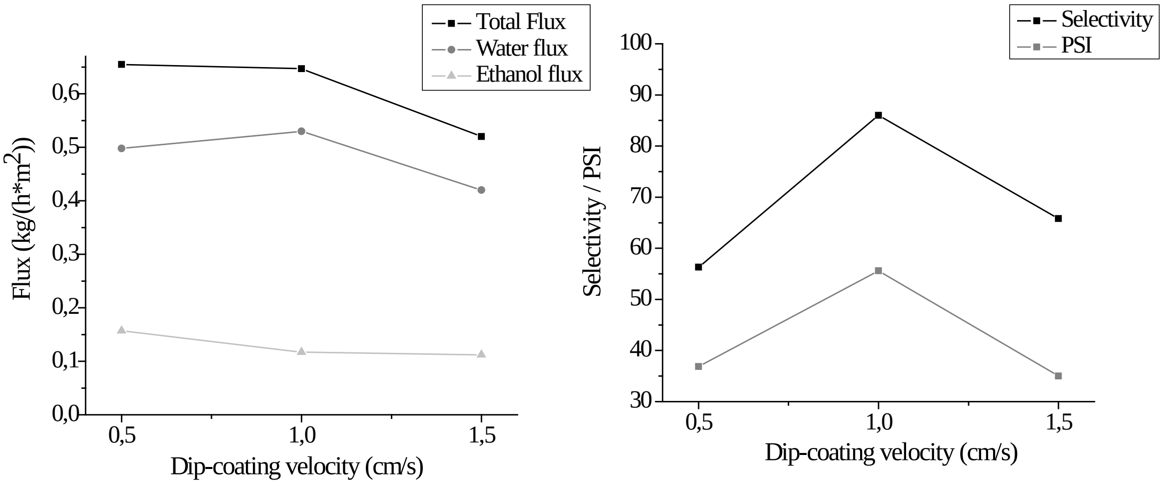


Figure 3-20. Performance of silica membranes deposited to dip-coating velocity of 0.5, 1 and 1.5cm.s^{-1}

Exists an optimum dip-coating velocity which can be used to deposit silica membranes (Figure 3-20), which is directly related to the silica thickness. Low deposition velocity causes thin silica films deposition. Moreover, high depositions velocity causes thick silica layer. Therefore, exist a more appropriated thickness to gives a good selectivity and flux value. Bonekamp et al. (2008) proposed that exists a critical layer thicknesses for pure silica layers, below this thickness microcracks of silica layer occur during drying and calcination process. It is probably that the thickness obtained with a dip-coating velocity of 0.5 cm.s^{-1} corresponds to the critical value, causing the lowest selectivity of the membranes studied.

Hydrophilic silica membrane deposited at dip-coating velocity of 1.5 cm.s^{-1} presents a reduction on total flux in comparison to the other studied membranes. The decrease in total flux can be related to the increase in silica thickness, causing more resistance to ethanol and water diffusion through the membrane. Moreover, the reduction in the selectivity of the studied membrane could be related to the decrease of water flux while the ethanol flux remained constants at the same value, comparing to the membrane deposited at 1cm.s^{-1}.

The application of a dip-coating velocity of 1 cm.s^{-1} let to obtain silica membrane characterized with better performance in pervaporation process: a total flux of 0,647 kg.m^{-2}h^{-1} with high selectivity (86) and therefore the highest PSI factor (56).

The strong effect of membrane calcination temperature on its performance in the pervaporation process was observed. Silica membranes calcined at 400, 450 and 500°C were tested in ethanol dehydration (5wt.%) at 70°C. Figure 3-21 presents the flux, selectivity and PSI of silica membranes calcined at different temperatures.

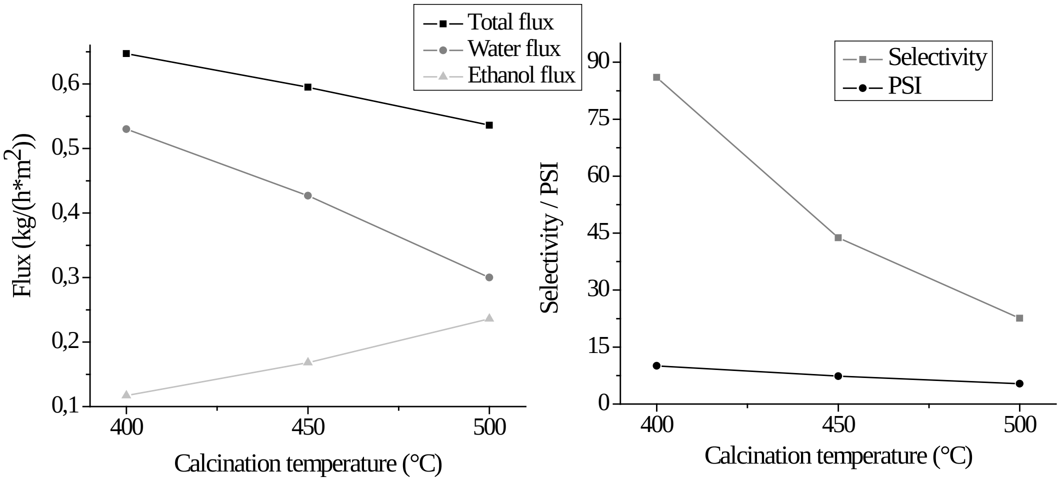


Figure 3-21. Performance of silica membranes calcined 400,450 and 500°C

Under increasing calcination temperature, the studied hydrophilic membranes present a continuous decrease in total and water flux (Figure 3-21); while the increase in the ethanol flux is observed. This could be related to the dehydroxylation of silica material at higher temperatures, as confirmed by TGA-DTA-MS and FTIR studies. The lost of silanol groups, which causes the hydrophilic nature of silica, leads to the decrease in water adsorption capacity and to the increase in organic molecules adsorption capacity. Therefore, selectivity to water decreases as the temperature is rised up to 500°C. Hence, silica membranes deposited at 1 cm.s^{-1} and calcined at 400°C presented the better pervaporation performance in ethanol dehydration in comparison with the others membranes prepared in this study.

In order to compare the performance of the prepared membranes in this study with the bibliographic data, the additional pervaporation experiment was performed for another concentration of ethanol-water mixture (6wt.% water, 94% ethanol) (Figure 3-22). The steady state was reached after 12 hours of pervaporation. The condition of stability was characterized by constant flux with error percentages of flux measurement less than 5% of three measurements consecutively.The obtained total final flux was 0,417 kg.m-2h-1, selectivity 207 and PSI 86. These values are one of the highest reported in the literature for ethanol dehydration (Table 3-8).

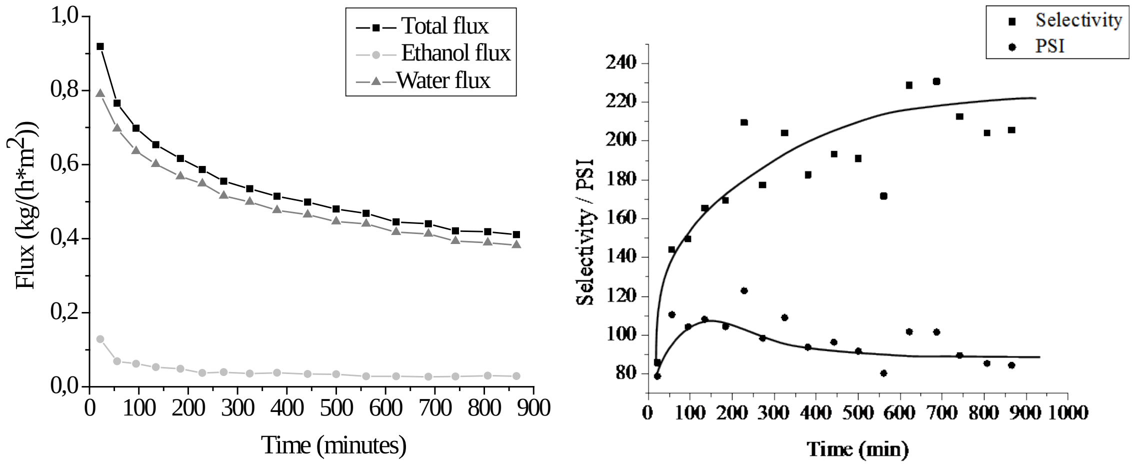


Figure 3-22. Flux, selectivity and PSI as time function in the ethanol dehydration (6wt% water) at 70°C

The separation performance of silica membranes prepared in this study was also compared, in the same experimental conditions, with commercial hollow fiber silica membranes (Hyflux CEPAration-Netherlands). Commercial membrane presented a PSI factor of 5 (selectivity of 12), lower than the value obtained for membranes prepared in this study (PSI 86). It confirms the successful preparation of defect free membranes with good ethanol dehydration performance in this study.

Table 3-8. Separation performance of silica membranes in ethanol dehydration

Water concentration (%)	**Feed permeate pressure (mbar)**	**Feed temperature (°C)**	**Total flux (kg.m^{-2}h^{-1})**	**Selectivity**	**PSI**	**Reference**
6	-	70	0,462	97	44	(Yu Ma et al.,2009)
6	-	70	0,761	358	272	(Yu Ma et al., 2009)
6	-	70	0,31	45	14	(Yu Ma et al., 2009)
6	-	70	0,728	20	14	(Yu Ma et al., 2009)
6,3	10	60	1,28	25	31	(Bettens et al., 2010)
6	3-5	70	0,432	12	5	Hyflux CEPAration
6	3-5	70	0,417	207	86	(This study)

Figure 3-23 presents the reduction of total flux, selectivity and PSI as function of membrane operation time. The decline in separation performance with time will be attributed to adsorption of ethanol by hydrogen bonding with hydroxyl groups on the silica surface, as was proposed in section 3.1.4. Adsorption of ethanol can render the silica more hydrophobic, reducing the water flux and selectivity and increasing the amount of ethanol passing through the membrane. A decline in flux with time has also been observed by Peters et al. (2005) in butanol dehydration.

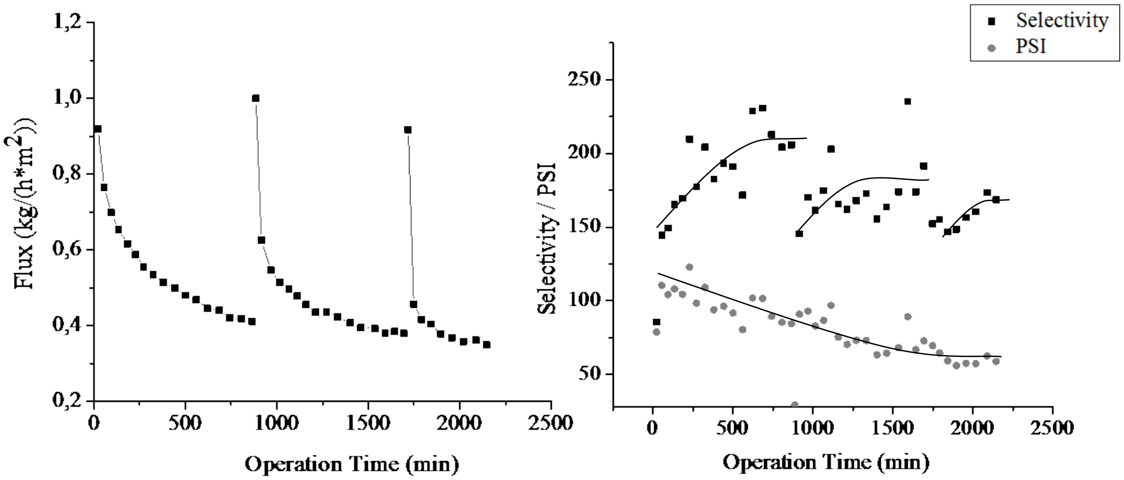


Figure 3-23. Hydrophilic silica membrane performance in ethanol dehydration (6wt.%water) by pervaporation at 70°C, in function of operation time.

The ethanol adsorption process is reversible due to the initial flux and selectivity of each pervaporation experiment have aproximately the same value. Nevertheless, the adsorption of ethanol during the pervaporation test has influence in the performance of the membrane to reach the steady stable.

The posible separation mechanism using hydrophilic silica membranes can be base on the hydrophilic nature of the membrane, in accordance with the adsorption–diffusion model (Sekulic et al., 2005), instead of pore size exclusion effect (Sommer & Melin, 2005). Hydrophilic silica powders were characterized with pore size of 17Ǻ, which is higher than the kinetic diameter of ethanol (4.4 Ǻ) and water (2.8 Ǻ) molecules. Therefore, it could be expected that both substances are able to diffuse through the membrane. Hydrophilic silica membrane calcined at 400°C, presented selectivity toward water in the separation process. Considering that it's hydrophilic nature was already confirmed (sections 3.1.2 and 3.1.4), it could be expected that selective pass of water through the membrane takes place.

3.1.6 Conclusions

- Hydrophilic silica xerogels synthesized by sol-gel method using the standard molar ratio TEOS (1): ethanol (3.8): water (6.4): nitric acid (0.085) are microporous materials (pore width 17Ǻ) with large specific surface area (> 500 $m^2.g^{-1}$).

- Aging process has influence on morphological properties of silica xerogel. Rough surface are obtained for the material aged during long time.

- Calcination process has a remarkable effect on silica properties, especially on the specific surface area and pore volume, which are reduced after calcination.

- The hydrophilic nature of silica surface generates the possibility of water and alcohols adsorption via hydrogen bonding. However, the hydrophilic nature of this material permits higher selectivity to water adsorption.

- The effect of dip-coating velocity and calcination temperature on the performance of silica membranes in ethanol dehydration was analyzed. Better performance in ethanol-water pervaporation was obtained for silica membranes deposited at 1 $cm.s^{-1}$ and calcined at 400°C.

- The hydrophilic nature of silica xerogels, allows their application as membrane for alcohol dehydration. High selectivity and PSI of 207 and 86, respectively was obtained for ethanol dehydration (6wt.% water) at 70°C. These values are one of the highest reported in the literature for ethanol dehydration.

3.2 Characterization of hydrophobic silica materials

Introduction

Textural, morphological, surface and adsorptive properties of hydrophobic silica xerogels, examined using BET, XRD, SEM, FTIR, and adsorption studies are presented in this section. Hydrophobic silica xerogels were prepared by co-precursor and derivatization methods, using TEOS: ethanol: water: HNO_3: hydrophobic agent molar ratio of 1:3.8:6.4:0.085:0.5. According to the literature (Venkateswara Rao & Kalesh, 2004), the application of methyltrimethoxysilane (MTMS) and methyltriethoxysilane (MTES) as a modifier agents leads to obtain microporous silica-based materials. Therefore, MTES and MTMS were chosen for hydrophobic silica xerogels preparation. Those hydrophobic agents cause the replacement of H from silanol groups by methyl groups, conferring hydrophobic properties to silica-based material.

The influence of the synthesis method, the type of hydrophobic agent and the calcination temperature on the properties of hydrophobic silica xerogels was investigated. Considering that alcogel aging plays an important role in the strengthening of silica network (chapter 3.1), all prepared samples where diluted in ethanol and aged during 15 days. The corresponding codification of the synthesized samples is presented in Table 3-9.

Furthermore, the thermal stability of synthesized hydrophobic material in air and argon atmosphere was performed using TGA-DTA-MS and FTIR techniques. The potential applications of hydrophobic silica xerogels are also proposed. Thus, their performance in the adsorption of alcohols and in the ethanol removal by pervaporation process is discussed. As far as we know, no similar adsorption and pervaporation studies on hydrophobic silica materials have been reported.

Table 3-9. Codification of hydrophobic silica xerogels

Sample	Hydrophobic agent	Synthesis method
S2	MTMS	Co-precursor
S3	MTMS	Derivatization
S5	MTES	Co-precursor
S6	MTES	Derivatization

3.2.1 Thermal stability

The TGA-DTA-MS analysis of hydrophobic, uncalcined silica xerogels, synthesized by two different methods (co-precursor and derivatization), using MTMS and MTES as hydrophobic agents, was applied to determine their thermal stability and the temperature range of their operation. Those studies were performed in two different atmospheres: air (oxidative) and argon (inert).

Figure 3-24 presents the thermogravimetric analysis (TGA) curves of hydrophobic silica xerogels, prepared by different methods, using MTMS or MTES as hydrophobic agents (Table 3-9), realized in a stream of air. Table 3-10 resumes the obtained results.

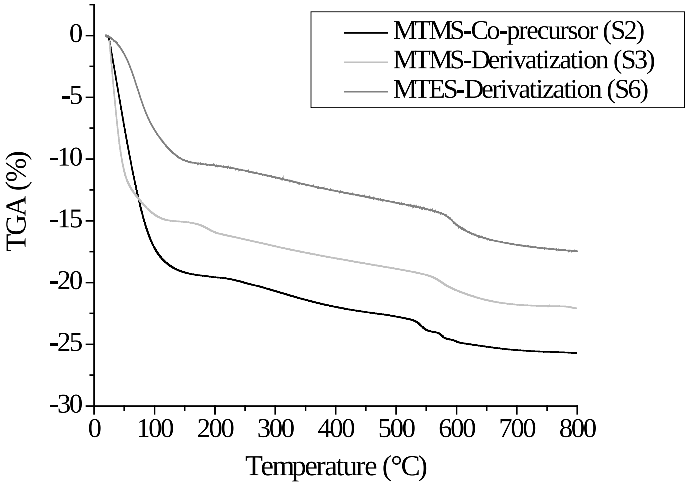


Figure 3-24. TGA curves of hydrophobic silica xerogels in air atmosphere

Table 3-10. The weight loss regions of hydrophobic silica xerogels in air atmosphere

Sample	**% Weight loss**			
	15-150°C	**150-500°C**	**500-800°C**	**Total**
MTMS-Co precursor (S2)	19	3	6	28
MTMS-Derivatization (S3)	15	3	6	24
MTES-Derivatization (S6)	10	3	7	20

One can see the significant effect of the synthesis procedure on the profile of TGA curves (Figure 3-24, sample S2 and S3). For the sample prepared by co-precursor method, a gradual decrease in weight loss with an increase in the temperature is observed (sample S2). However, in the case of derivatizated xerogel (sample S3), a sharp decrease in weight loss with an increase in the temperature is seen. The experimented difference seems to be related to the details of the preparation procedure and their effect on materials properties. In the case of the xerogels prepared by co-precursor method, the hydrophobic reagent was added to the sol itself and consequently hydrolytically stable groups get attached to the inner silica clusters as well as the surface clusters and hence structural changes took place. On the other hand, in the case of derivatizated xerogel, only the surface SiO_2 clusters get modified.

In order to explain the performance of the hydrophobic silica xerogels under increasing temperature, the differential thermal analysis (DTA) and mass spectrometry (MS) studies were also performed. The representative TGA-DTA curves obtained for one of the studied samples (S6), in air atmosphere, are presented in Figure 3-25. Table 3-13 summarizes corresponding response of MS, coupled with TGA-DTA analysis. Similar results were also obtained for the other hydrophobic silica xerogels.

Independent of the synthesis conditions, the TGA thermograms of hydrophobic silica xerogels (Figure 3-24) obtained in air exhibit three main regions of weight loss (Table 3-10). Through the first weight loss region of 10-20%, depending on the synthesis procedure, in the temperature range 15-150°C, desorption of physically adsorbed and/or trapped in the xerogel network water and ethanol occurs, as confirmed by MS studies (Table 3-11). The presence of both an endothermic peak in the DTA curve (Figure 3-25 a), with the maximum at ca. 70°C, and OH^+ (m/z=17), H_2O^+ (m/z=18), $C_2H_3O^+$ (m/z=43) species in the MS spectrum, with the maximum at ca. 110°C, confirms the observed effects. Moreover, decomposition of the residual nitric acid, used as a catalyst during the xerogel synthesis, with a maximum at ca. 135°C, is observed (Table 3-11). The second weight loss region of ca. 3%, in the temperature range 150°C-500°C, could be assigned to the removal of residual organic compounds (specially ethoxy groups from TEOS) and the release of water adsorbed inside the small pores of silica xerogel (Venkateswara Rao et al., 2003). The presence of H_2O^+(m/z=18) and CO_2^+ (m/z=44) species in the MS spectrum at 150-230°C and 450-500°C, respectively confirms desorption of chemisorbed water and TEOS decomposition.

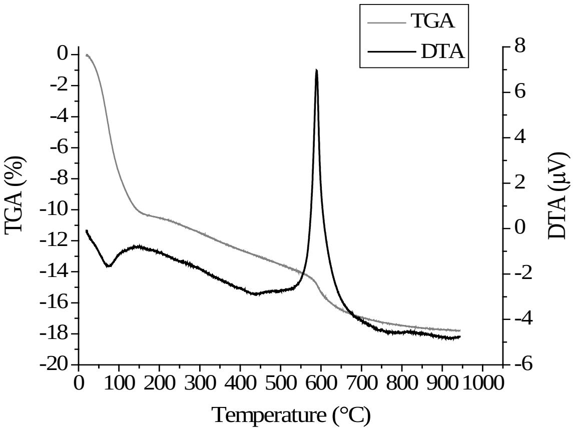


Figure 3-25. TGA-DTA studies of hydrophobic silica xerogel (sample S6) in different atmosphere: a) air, b) argon

The further weight loss of ca. 6%, at temperature above 500°C, is related to the oxidation of methyl groups presented on silica surface into OH groups, as confirmed by MS studies (CO_2^+ (m/z 44) and H_2O^+ (m/z 18) species with maximum at 590°C). Moreover, for MTES modified silica xerogel (sample 6), an exothermic peak with a maximum at 590°C is observed, confirming the possible combustion of methyl groups presented on silica surface. In the temperature range 420-700°C, the presence of CH_3^+ species (m/z=15) was also registered by MS, suggesting also the release of methyl groups from silica surface. Therefore, the hydrophobicity of the silica xerogels in air atmosphere is retained up 570°C for xerogels synthesized with MTMS and up to 590°C for materials prepared with MTES. Above these temperatures, the silica xerogels becomes hydrophilic. The slight difference in the temperature of methyl groups' oxidation can be attributed to the slight changes in the bond length due to difference in the structural formula of the silylating agents (MTMS and MTES). At 900°C, the total weight loss of hydrophobic silica xerogels is about 24%.

Table 3-11. The summary of MS results for hydrophobic silica xerogel (sample S6) in air atmosphere

Mass number (m/z)	Temperature (max. intensity) (°C)	Temperature range (°C)	Intensity ion current (A)	Key fragments	Probable parent molecule
15	590	420-700	7,70x10^{-7}	CH_3^+	C_xH_y
17	110	20-200	2,62 x10^{-6}	OH^+	H_2O
17	595	540-710	2,06 x10^{-7}	OH^+	H_2O
18	110	20-230	1,18 x10^{-5}	H_2O^+	H_2O
18	590	520-715	2,06 x10^{-6}	H_2O^+	H_2O
43	135	20-230	1,96 x10^{-8}	$C_2H_3O^+$	C_2H_5OH
44	590	450-700	1,50 x10^{-6}	CO_2^+	CO_2
46	135	60-290	2,84 x10^{-8}	NO_2^+	NO_2

In order to confirm the phenomena observed during the thermal treatment of hydrophobic silica xerogels in air atmosphere, in situ FTIR studies with the programmed increase in the temperature were also performed. Figure 3-26 depicts the representative FTIR spectra of uncalcined, silica xerogel synthesized by derivatization method, using MTMS or MTES as hydrophobic agents (samples S3 and S6), recorded in the temperature range 20-400°C, in air atmosphere. The identified bands in the silica spectra are summarized in Table 3-12.

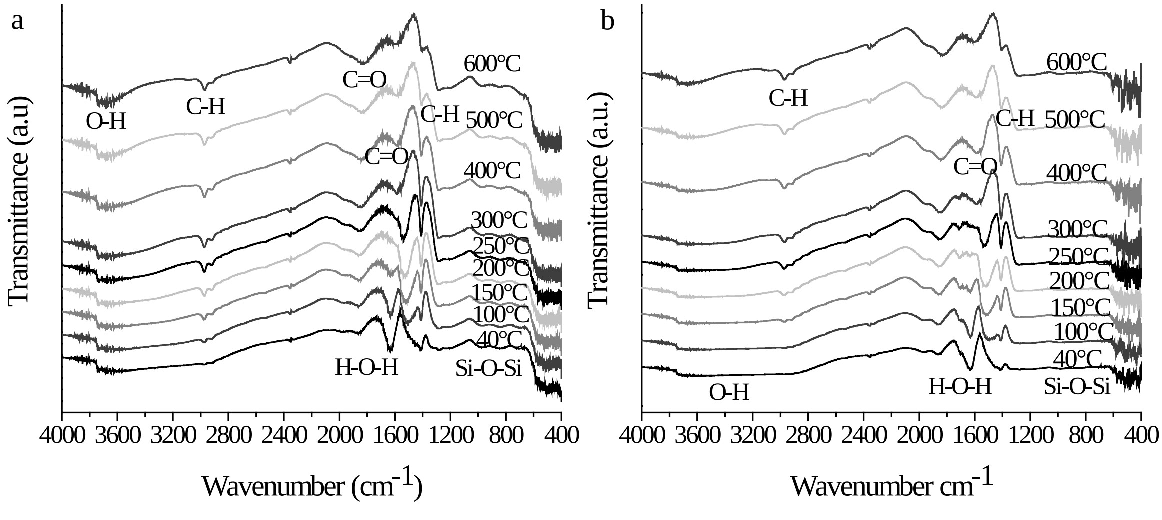


Figure 3-26. The influence of the temperature on the FTIR spectra of uncalcined, hydrophobic silica xerogel prepared by derivatization method using a) MTMS (sample S3) and b) MTES (sample S6) as hydrophobic agents

Table 3-12. Characteristic vibration frequencies in FTIR spectra of hydrophobic silica xerogels realized under increasing temperature

Vibration type	Structural unit	Wavenumber (cm^{-1})		References
		Silica synthesized with MTMS	Silica synthesized with MTES	
O-H	H-O-H…H_2O	3725-3380	3712-3414	(Al-Oweini & El-Rassy 2009)
ν_{as} C-H	CH_2	2981	2970	(Al-Oweini & El-Rassy 2009)
ν_s C-H	CH_2	2912	2895	(Al-Oweini & El-Rassy 2009)
C=O	CO_2	2340	2362	(Socrates 1994)
C=O	Carbonyl Groups	1840	1849	(Socrates 1994)
δ H-O-H	H_2O	1641	1640	(Al-Oweini & El-Rassy 2009)
C=O	Carbonyl Groups	1544	1530	(Socrates 1994; Stuart 2004)
C-H	Si-R	1419	1410	(Al-Oweini & El-Rassy 2009)
ν_{as} Si-O-Si	Si-O-Si	1246-692	1306-600	(Al-Oweini & El-Rassy 2009; Socrates 1994)

δ: Deformation vibration, δ_{as}: Antisymmetric deformation vibration, δ_s: Symmetric deformation vibration, ν: Stretching vibration, ν_{as}: Antisymmetric stretching vibration,ν_s: Symmetric stretching vibration,ν_β: In-plane stretching vibration.

The FTIR spectra of the studied hydrophobic silica xerogels show bands in the range of 3725-3160cm^{-1} and 1200-650 cm^{-1}, which can be assigned to the O-H and Si-O-Si interactions, respectively, characteristic for silica.

At 1640 cm^{-1}, an intense band associated with water adsorption on the surface of the sample is observed. Its intensity significantly decreases with an increasing temperature up to 200°C. Above this temperature 200°C this band disappears. TEOS thermal decomposition in air atmosphere was also evidenced by FTIR experiments, at temperatures higher than 250°C. The presence of new interaction bands C=O, associated to species released during thermal decomposition, are evidenced at ca. 1840 cm-^{1} and ca.1544 cm^{-1} for hydrophobic silica at 250°C.

The first indication of the successful modification of silica surface is the absence of isolated hydroxyl groups, normally present at ca. 3740cm^{-1}. Moreover, the presence of the new bands at 1419 cm^{-1} and 1410 cm^{-1} in the silica xerogels, synthesized using MTMS and MTES as hydrophobic agents, respectively confirms its hydrophobic nature. These bands are associated with the C-H interaction of Si-R structure units, where R is the methyl groups attached to silica surface during modification process. The intensity of new bands increases with increase in the temperature up to 500°C. Above this temperature, their intensity gradually decreases. Therefore, those studies confirm the thermal stability of hydrophobic silica xerogels up to 500°C. At higher temperature silica starts to demonstrate again its hydrophilic character.

Therefore, basing on the TG-DTA-MS and in situ FTIR studies, it could be expected that exists a temperature limit at which hydrophobic silica xerogels can be calcined to conserve their hydrophobic character. Above this temperature, the material returns to hydrophilic nature. Independent of the synthesis procedure and hydrophobic agent used for the preparation, the obtained silica xerogels present thermal stability up to ca. 500°C. It should be noted that this temperature value is the highest one reported for silica-based materials, modified with MTMS and MTES hydrophobic agents. According with the literature (Venkateswara Rao & Bhagat, 2006; Venkateswara Rao & Kalesh, 2004), silica aerogels modified with MTMS and MTES by co-precursor method retain their hydrophobicity at temperature below 270°C.

3.2.2 Surface characterization

Silica surface characterization was performed by FTIR spectroscopy. The comparison of hydrophilic and hydrophobic silica FTIR spectra obtained for some of the studied samples (sample M1, S2, S5, Table 3-1 and Table 3-9) calcined in air at 400°C, are presented in Figure 3-27. A complete list of the vibration frequencies and their assignments for FTIR spectra are presented in Table 3-13.

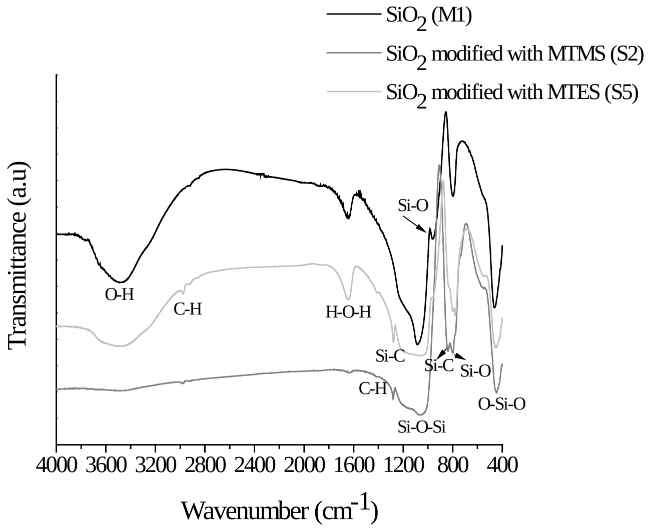


Figure 3-27. FTIR spectra of hydrophilic (sample M1) and hydrophobic silica xerogel (samples S2, S5)

The typical stretching vibration of silica are presented in the range of 1200–1000 cm^{-1}, and are attributed to silicon-oxygen covalent bonds (Si–O–Si) which reveal the existence of a dense silica network. The other bands at 1060 and 800 cm^{-1}, corresponding to asymmetric and symmetric stretching of Si-O-Si, and the band at 460 cm^{-1}, assigned to deformation vibration of O-Si-O are observed both in the hydrophilic and hydrophobic silica spectra.

The hydrophilic nature of unmodified silica is attributed to the presence of hydroxyl groups (-OH) on silica surface. These groups are evidenced in FTIR spectra as a broad band at 3400-3500cm^{-1}. This characteristic bands can be related to the presence of O-H stretching bands, caused by hydrogen-bonded water molecules (H-O-H …H) and surface silanol groups, hydrogen-bonded to the molecular water (SiO-H…H_2O) (Czarnobaj, 2008). Moreover, the hydrophilic nature of the silica material can be correlated with the band at 1640 cm^{-1}, corresponding to the water vibration adsorbed on silica surface (Parvathy Rao et al., 2005b) and at 960cm^{-1}, assigned to Si-O in plane stretching vibrations of the silanol (Si-OH) group (Al-Oweini & El-Rassy, 2009).

Table 3-13. Characteristic vibration frequencies in FTIR spectra of hydrophilic silica xerogel

Wavenumber (cm^{-1})	**Band Assigment**	**Structural Unit**	**Reference**
3748	Si-OH	Si-OH	(Takei, 1999)
3480	H-O, SiO-H	H-O-H…H_2O and SiO-H…H_2O	(Al-Oweini & El-Rassy, 2009)
2970	ν_s C-H	$-CH_3$	(Al-Oweini & El-Rassy, 2009)
2940	ν_{as} C-H	$-CH_2$	(Al-Oweini & El-Rassy, 2009)
1883	ν_β Si-O	Si-OH	(Lucousky & Pollard, 1983)
1640	δ H-O-H	H-O-H	(Al-Oweini & El-Rassy, 2009)
1400	δ_s C-H	$-CH_3$	(Al-Oweini & El-Rassy, 2009)
1380	ν_s C-H	$\equiv Si{-}O{-}C_2H_5$	(Socrates, 1994)
1279	ν Si-C	$Si{-}CH_3$	(Al-Oweini & El-Rassy, 2009)
1060	ν_{as} Si-O-Si	Si-O-Si	(Araujo-Andrade & Martínez, 2000)
968	ν_β Si-O	Si-OH	(Al-Oweini & El-Rassy, 2009)
840	ν Si-C	$Si{-}CH_3$	(Al-Oweini & El-Rassy, 2009)
800	ν_s Si-O	Si-O-Si	(Al-Oweini & El-Rassy, 2009)
674	ν_s Si-O-Si	Si-O-Si	(Al-Oweini & El-Rassy, 2009)
576	ν Si-O	SiO_2 Defects	(Al-Oweini & El-Rassy, 2009)
460	δ O-Si-O	O-Si-O	(Socrates, 1994)

δ: Deformation vibration, δ_{as}: Antisymmetric deformation vibration, δ_s: Symmetric deformation vibration, ν: Stretching vibration, ν_{as}: Antisymmetric stretching vibration,ν_s: Symmetric stretching vibration,ν_β: In-plane stretching vibration.

Chemical modification of silica is confirmed by the presence of the bands at 1279 and 840 cm^{-1} attributed to Si–C stretching vibrations (Cui et al., 2011). These bands are characteristic only for modified silica. Moreover, the bands observed at 2970 and 1400 cm^{-1}, which represent the symmetric stretching vibration and asymmetric deformation vibration of C-H, specially attributed to methyl groups (Al-Oweini & El-Rassy, 2009) also ratify the silica modification. Those groups are attached to silica surface during the modification with MTMS and MTES hydrophobic agent.

A decrease in intensity of the band related to water adsorption (1640 cm^{-1}) for silica xerogel modified with MTMS, in comparison to the hydrophilic silica and silica modified with MTES, were observed. This fact indicates the hydrophobic character of modified material and suggest that a better surface and bulk modification is performed using the hydrophobic agent MTMS.

Figure 3-28 (a) presents the FTIR spectra of silica xerogel prepared by derivatization and co-precursor method (samples S1 and S3), using MTMS as hydrophobic agent, calcined. Lower intensity of the characteristic bands related to both the hydroxyl groups (3480 cm^{-1}) and water adsorption on silica surface (1640 cm^{-1}), for sample synthesized by co-precursor method, can be observed. Moreover, the presence of a well defined band at 840 cm^{-1}, related to the Si-C bonds, suggests that modification with MTMS by co-precursor method gives silica xerogel characterized with higher degree of hydrophobicity. On the other hand, the presence of interaction at 960 cm^{-1}, related to the in plane stretching vibration of Si-O associated to silanol groups (Si-OH), in FTIR spectra of silica xerogel synthesized using MTES by co-precursor method (Figure 3-33 b) suggests that more effective modification can be obtained by derivatization method with MTES hydrophobic agent.

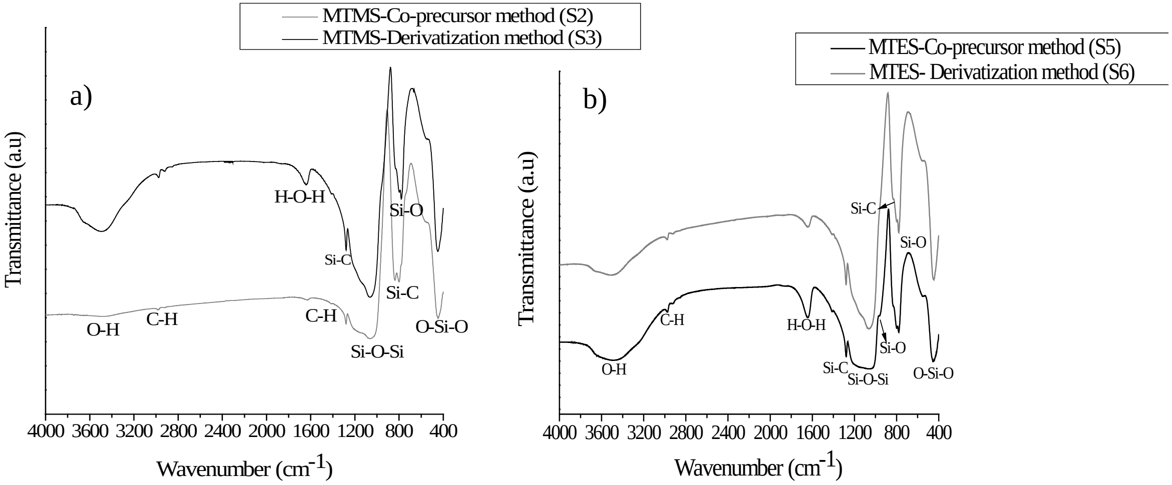


Figure 3-28. FTIR spectra of silica xerogel synthesized by co-precursor and derivatization methods, using a) MTMS and b) MTES hydrophobic agents and calcined (samples (S2, S3, S5, S6)

In order to confirm the chemical modification of silica xerogels and the thermal stability of hydrophobic materials, FTIR spectra were recorded after their calcination at different temperatures. Figure 3-29 and Figure 3-30 presents FTIR spectra of silica xerogels synthesized by co-precursor and derivatization method, using MTMS or MTES as hydrophobic agents.

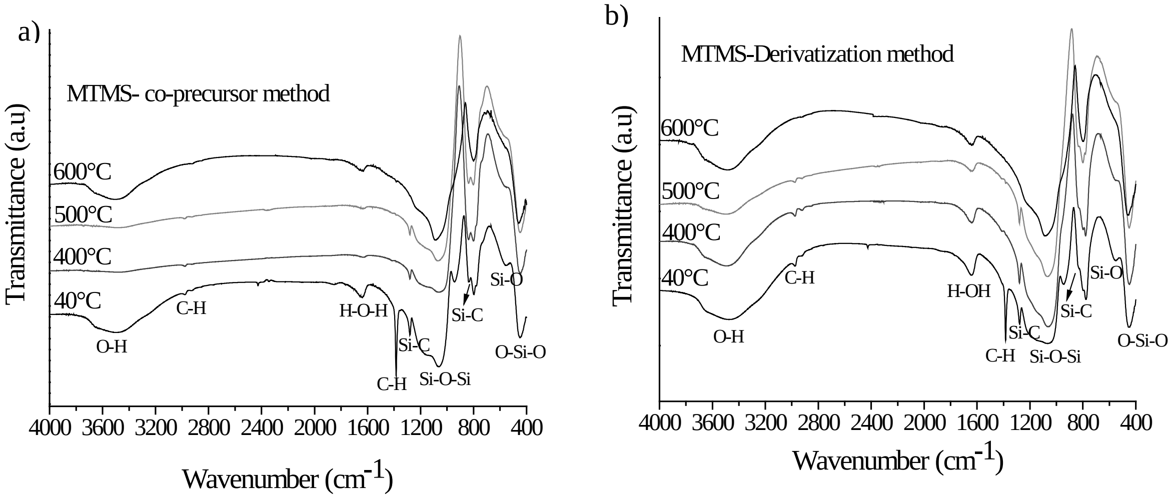


Figure 3-29. FTIR spectra of silica xereogels synthesized by: a) co-precursor method (sample S2) and b) derivatization method (sample S3), using MTMS, and calcined at different temperatures

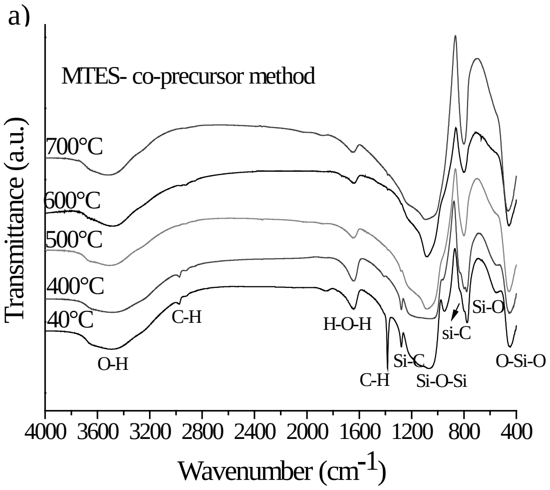


Figure 3-30. FTIR spectra of silica xereogels synthesized by: a) co-precursor method (sample S5) and b) derivatization method (sample S6), using MTES, and calcined at different temperatures

Silica xerogels synthesized by MTMS and MTES by co-precursor and derivatization method, and dried at 40°C exhibit a characteristic band at 1380 cm^{-1} which is not present in calcined samples. This band is attributed to ≡Si–O–C_2H_5 interaction associated with the presence of residual TEOS. On the other hand, the presence of Si-O interaction at 940 cm^{-1} and the higher intensity of the band at 3480cm^{-1} related to the isolated hydroxyl groups (-OH) in dried samples, suggests that higher hydrophobic character is obtained after calcination, when silica xerogel densification is achieved.
Silica xerogels prepared by co-precursor and derivatization method, using MTMS and MTES as hydrophobic agents, calcined at 400°C and 500°C presents a hydrophobic character. The presence of Si-C interactions at 1279 and 840 cm^{-1} confirms the silica modification.

The increase in the calcination temperature up to 600°C and 750°C for silica xerogel modified with MTMS and MTES, respectively generates the loss of hydrophobicity, due to the oxidation of methyl groups incorporated during silica modification. Consequently, the absence of interactions at 1279 and 840 cm^{-1}, associated to Si-C interactions, and the increase in the band intensity of hydroxyl groups' interactions, at 3400-3500 cm^{-1}, is observed.

Therefore, the thermal stability of hydrophobic silica xerogels synthesized by co-precursor and derivatization method, using MTMS and MTES as hydrophobic agents, is only guaranteed in the samples calcined below 500°C. This result is in agreement with the thermal stability obtained by TGA-DTA measurement of 570°C for silica gel modified with MTMS and 590°C for material modified with MTES.

As it was mentioned above, during the preparation of silica xerogels by derivatization method (washing step), the presence of some particles in the obtained xerogel was observed. In order to know the composition of those particles, FTIR studies of both solid phases (gel and particles) were performed. Figure 3-31presents the FTIR spectra of silica xerogel prepared by derivatization method, using MTMS (sample S3) and the particles separated during the modification. A new band at 1377 cm^{-1}, assigned to C-H interactions, is only observed in the case of separated particles. This interaction band can be related to the unreacted and trapped organic compounds, especially MTMS, which were removed during washing procedure. The band observed in the range of 1200-1000 cm^{-1}, assigned to symmetric Si–O–Si stretching vibrations characteristic for silica, are presented in both samples. This indicates that the separation of particles by decantation is not an effective method to remove the modified gel and the washing products.

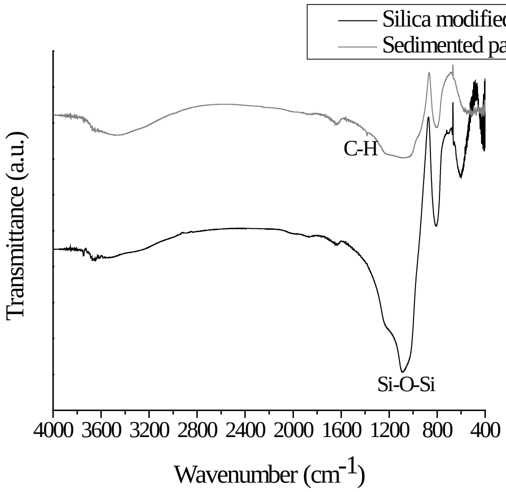


Figure 3-31. FTIR spectra of hydrophobic silica obtained by derivatization method using MTMS as hydrophobic agent (sample S3) and separated particles.

3.2.3 Textural and morphological properties

Textural and morphological properties of the hydrophobic silica xerogels were studied by SEM-EDS, N_2 physisorption and XRD techniques. The influence of parameters such as: the type of hydrophobic agent, preparation method and calcination temperature on the textural and morphological properties of synthesized hydrophobic silica was determined.

SEM micrographs of calcined silica xerogel prepared by derivatization and co-precursor method, using MTMS and MTES are presented in Figure 3- 32. Different morphology of hydrophobic silica xerogels depending on the applied preparation method is observed. Independent of the type of applied hydrophobic agent, one can see a smooth surface with some superficial defects (as marked in the corresponding micrograph, Figure 3- 32) when silica xerogeles was synthesized by co-precursor method. On the other hand, for the sample prepared by derivatization method more irregular and imperfect surface of xerogel, with some characteristic mounds and superficial defects, is observed. Characteristic morphological heterogeneity of the surface is also observed for silica modified (sample S3) as well as for the sedimented particles.

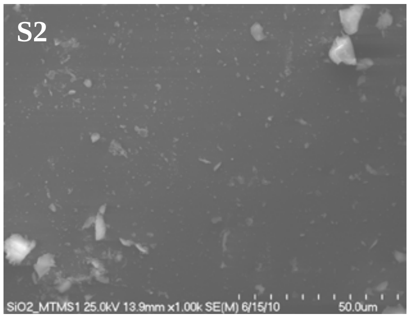
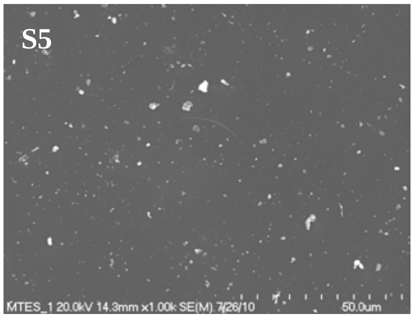
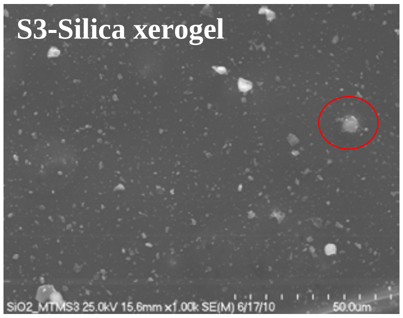
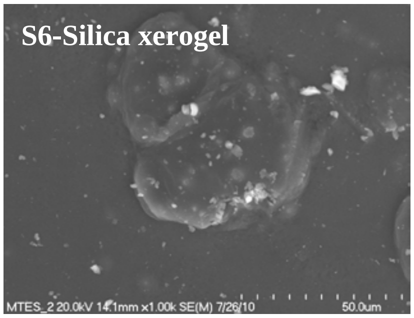
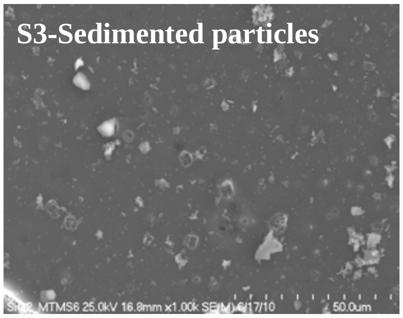
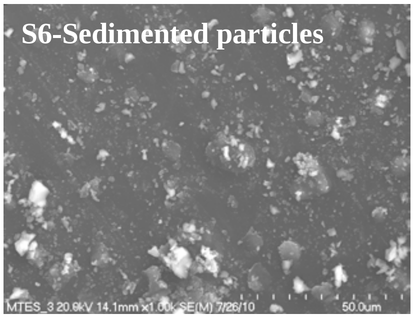
	MTMS	**MTES**
Co-precursor method		
Derivatization method (Modified silica)		
Derivatization method (Sedimented particles)		

Figure 3- 32. SEM micrographs of hydrophobic silica xerogel calcined. Magnification x 1000

The separation of modified silica xerogel and particles is an important step in derivatization method, if this separation is not effective, big morphological and textural differences can be presents, as is shown in Figure 3-33.

One can see two characteristic layers on the surface of silica gel prepared by derivatization method, using MTMS (Figure 3-33). The top layer (white color) is attributed to silica xerogel and the bottom one (gray color) is related to the sedimented particles which were not removed effectively during the washing procedure and posterior sedimentation process. Morphological similarities of bottom layer (Figure 3-33a) and particles (Figure 3-33) is observed in SEM micrograph.

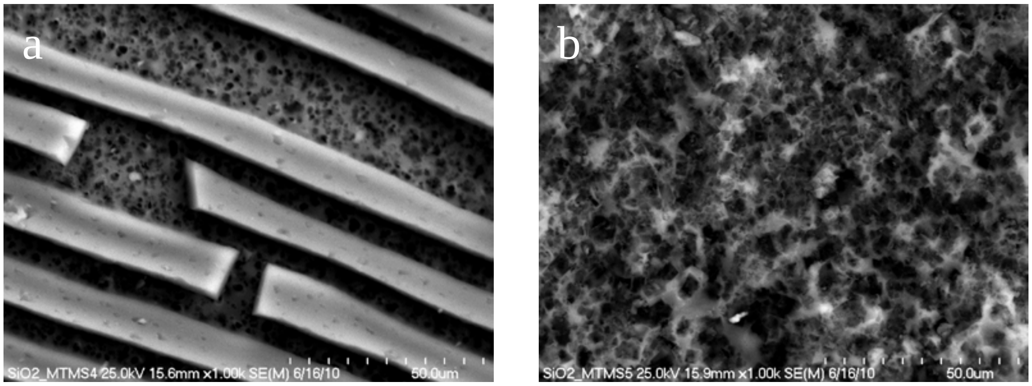


Figure 3-33. Silica xerogel prepared by derivatization method, using MTMS (Sample S3) as modifier agent, calcined a) silica xerogel, b) sedimented particles

The N_2-physisorption studies over hydrophobic silica xerogels were applied to determine their textural properties. The N_2-adsorption isotherms obtained at 77 K for hydrophobic silica xerogels synthesized by co-precursor and derivatization method (samples S2, S3, S5 and S6), calcined , are depicted in Figure 3-34(a).

In the case of silica synthesized by derivatization method, independent of the type of the hydrophobic agent, as well as for silica prepared by co-precursor method, using MTMS exhibits a high nitrogen adsorption at very low relative pressure. This kind of behavior is characteristic for adsorption isotherm type I (Khalfaoui et al., 2003), which corresponds to a microporous material. However, the N_2-adosorptive performance of silica prepared by co-precursor method, using MTES, can be described as adsorption isotherm type IV (Khalfaoui et al., 2003), characteristic for mesoporous material.

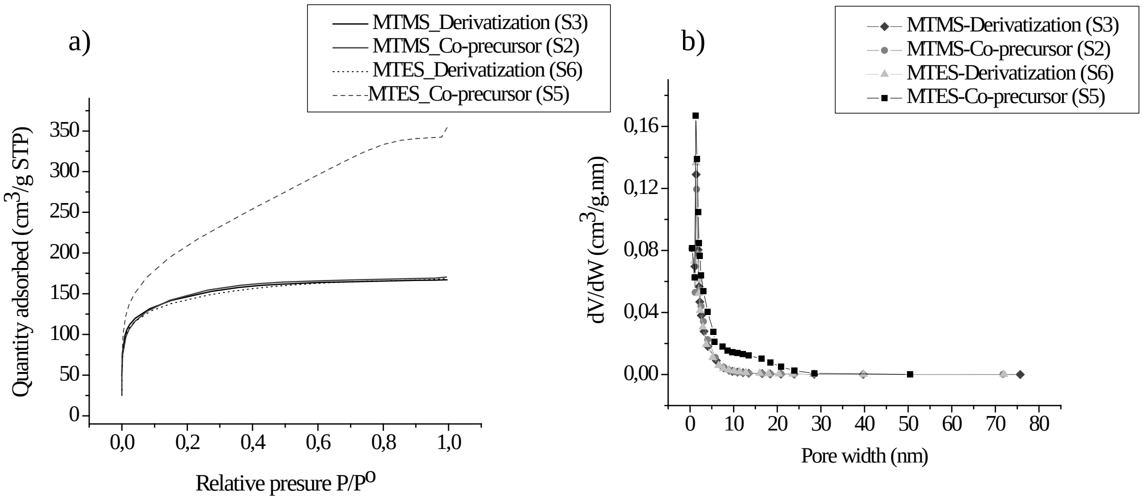


Figure 3-34. N_2-adsorption results: a) Adsorption isotherms at 77K for hydrophobic silica xerogels, synthesized under different conditions (S2,S3,S5,S6) and calcined; b) Pore size distribution calculated using Horvath-Kawazoe model

Figure 3-34 (b) presents the representative micropore size distribution, calculated by the Horvath-Kawazoe method (Horvath & Kawazoe, 1983), obtained for the studied samples (S2, S3, S5 and S6). In general, the pore size distribution is narrow and uniform due to the presence of small size SiO_2 particles and pores. Nevertheless, the pore size distribution of silica xerogel synthesized by co-precursor method, using MTES, is shifted toward larger pore width. The principal surface parameters of the hydrophobic silica xerogels, examined by N_2-adsorption are presented in Table 3-14.

Table 3-14. Specific surface area, pore volume, porosity and pore width calculated by Horvath-Kawazoe method for hydrophobic silica xerogels, synthesized under different conditions (S2, S3, S5 and S6)

Sample	Specific surface area BET (m^2/g)	Maximum pore volume (cm^3/g)	Average pore width(Å)	Porosity
MTMS-Derivatization-400°C (S3)	487	0,2585	16	36,3
MTMS-Co-precursor-400°C (S2)	502	0,2638	17	36,7
MTES-Derivatization-400°C (S6)	479	0,2608	16	36,5
MTES-Co-precursor-400°C (S5)	739	0,5298	32	53,8

Similar specific surface area, pore volume and pore width were observed for silica xerogel prepared by co-precursor and derivatization methods, using MTMS as hydrophobic agents as well as for the sample prepared by derivatization method, using MTES. The introduction of organic groups as CH_3 on the surface of silica xerogel by derivatization method hardly affects the particles and pore size in comparison with hydrophilic silica xerogel. This is because the silica particles are primarily formed by hydrolysis and condensation of TEOS whereas the MTMS or MTES units subsequently hydrolyzed and condense on the particle surface. Therefore, microporous materials were achieved after modification of silica xerogel by derivatization method with methyl groups from MTES and MTMS.

The strong effect of the type of the hydrophobic agent on the textural properties of the silica xerogels synthesized by co-precursor method could be attributed to differences in hydrolysis rate of MTMS and MTES, in comparison to TEOS.

Calcination process clearly influences the textural properties of hydrophobic silica xerogel synthesized by co-precursor method, using MTMS (sample S2). Specific surface area, pore volume and porosity results are summarized in Table 3-15. The reduction of pore volume observed for hydrophobic silica xerogel modified with MTMS and calcined at 600°C can be attributed to the oxidation of Si-CH3 groups on the gel surface to Si–OH, at temperature above 570°C, causing the pores contraction. The equal results of pore width exhibited for analyzed sample (S2), calcined at different temperatures, is associated with the average obtained of the pores width presents on the sample; obtaining a media data of pore width calculated from isotherm by means Horvath-Kawazoe equation using cylinder Pore Geometry.

Table 3-15. Specific surface area, pore volume, porosity and pore width calculated by Horvath-Kawazoe method for hydrophobic silica xerogels (sample S2), calcined at 400°C and 600°C

Sample	Specific surface area BET (m^2/g)	Pore volume (cm^3/g)	Average pore width (Å)	Porosity
MTMS-Co-precursor-400°C (S2)	502	0,2638	17	36,7
MTMS-Co-precursor-600°C (S2)	224	0,1147	17	20,1

Basing on the X-ray diffraction studies (Figure 3-35), the amorphous character of the studied hydrophobic silica xerogels was confirmed. The XRD pattern exhibited only broad humps in the range of 2θ: 15-30° (Czarnobaj, 2008).

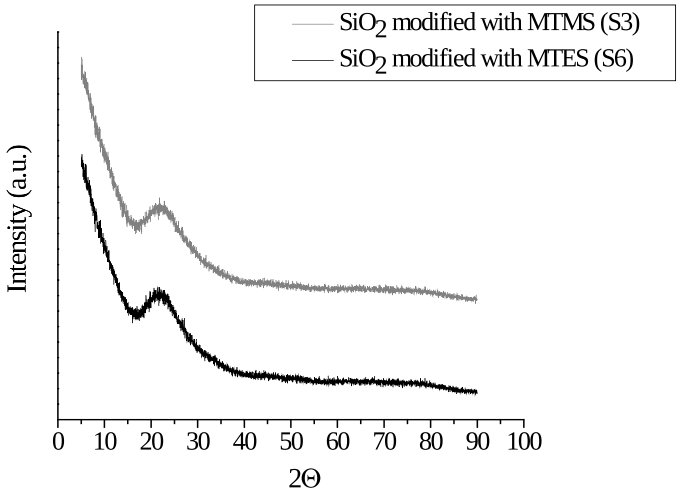


Figure 3-35. X-ray diffraction patterns of hydrophobic silica xerogels calcined at 400°C (samples S3 and S6)

3.2.4 Adsorptive properties

The adsorption studies over silica xerogels were performed in two different modes: in the liquid and gaseous phases, over hydrophilic silica xerogel (sample M1) and several hydrophobic silica xerogels synthesized under different conditions (S2, S3, S5 and S6).

The adsorption studies of pure ethanol, water and their mixture (95wt.% H_2O, 5wt.%C_2H_5OH) in liquid phase were performed, in order to select the most hydrophobic material synthesized. The taken criterion was the highest ethanol adsorption capacity. Hydrophobic silica xerogel modified by co-precursor and derivatization method, using MTMS and MTES were used as adsorbents. Only the samples prepared by co-precursor method, at initial hydrolysis temperature of 5°C were analyzed (sample S2 and S5). These samples were selected considering that the initial hydrolysis temperature has only influence on the textural and morphological properties of hydrophobic silica materials, as confirmed by SEM and specific surface area measurements (section 3.2.3).

Figure 3-36 shows the behavior of hydrophilic and hydrophobic silica xerogels in ethanol and water adsorption. Table 3-16 reports the codification of studied samples and their adsorption capacities.

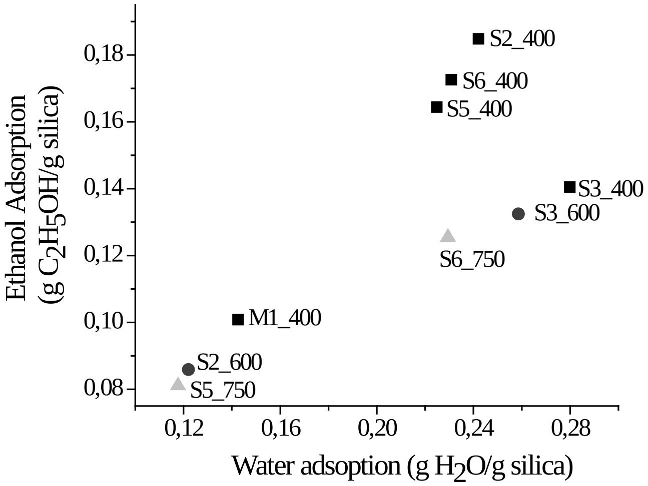


Figure 3-36. Ethanol and water adsorption capacity of hydrophilic and hydrophobic silica xerogels, units: g adsorbate / g silica

Table 3-16. Codification of silica xerogels studied in ethanol and water adsorption, ethanol and water adsorption capacities

Sample	Modifier Agent	Method of modification	Calcination temperature (°C)	Ethanol adsorbed (g EtOH /g silica)	Water adsorbed (g Water /g silica)
M1_400	-	-	400	0,0967	0,1426
S2_400	MTMS	Co-precursor	400	0,1848	0,2421
S3_400	MTMS	Derivatization	400	0,1405	0,2799
S2_600	MTMS	Co-precursor	600	0,0859	0,122
S3_600	MTMS	Derivatization	600	0,1324	0,2586
S5_400	MTES	Co-precursor	400	0,1644	0,2249
S6_400	MTES	Derivatization	400	0,1726	0,2309
S5_750	MTES	Co-precursor	750	0,0811	0,1177
S6_750	MTES	Derivatization	750	0,1255	0,2295

One can see that calcination temperature has strong influence on the adsorptive properties of hydrophobic silica xerogels. Hydrophobic samples calcined at 400°C presents higher ethanol adsorption capacity in comparison to the samples calcined at 600°C and 750°C. The observed decrease in the ethanol adsorption capacity is related with the gradual loss of hydrophobic nature of the studied materials, at temperatures above 500°C, as also confirmed by TGA and FTIR studies (sections 3.2.1 and 3.2.2).

It was observed that the replacement of hydroxyl groups by methyl groups from MTMS and MTES hydrophobic agents by co-precursor and derivatization method, changes the hydrophilic nature of the silica. Therefore, the ethanol adsorption capacity is much higher for modified samples (S2, S3, S5 and S6) than that for hydrophilic one (M1), all of them calcined at 400 °C. The presence of methyl groups, which confers the hydrophobic character, was also confirmed by FTIR measurements for silica samples synthesized by co-precursor and derivatization method using both hydrophobic agents (section 3.2.2).

More effective modification with MTMS is achieved using the co-precursor method (S2_400) in contrast to the derivatization method (S3_400). It is supported by higher ethanol adsorption capacities obtained by co-precursor synthesized xerogel. It could be related to the modification grade achieve by different methods. The application of co-precursor method leads to the modification of both bulk and surface clusters of silica, giving more hydrophobic character to the material. On the other hand, using derivatization method, only the surface SiO_2 clusters get modified. More hydrophobic nature of silica material synthesized by co-precursor method was also suggested basing on the obtained FTIR results (section 3.2.2)

One can see that the lowest ethanol and water adsorption capacity is presented by silica xerogels prepared by co-precursor method, using MTMS (S2_600) and MTES (S5_750), and calcined at 600°C and 750°C, respectively. This could be related to the fact that the thermal treatment of the studied samples at higher temperature causes the loss of hydrophobicity and the reduction of pore volume and specific surface area, as confirmed by FTIR and N_2-physisorption studies (section 3.2.3). Especially the material modified by co-precursor method suffers drastic changes due to the modification nature (bulk and surface silica clusters).

Silica xerogel synthesized by co-precursor method, using MTMS as hydrophobic agent and calcined at 400°C (Sample S2_400) is the sample which presented the highest ethanol adsorption capacity. Hence, it could be suggested that the chemical modification of silica xerogel by co-precursor method, using MTMS produces more hydrophobic silica materials, in comparison with other methods and modifier agents. Similar results were obtained by FTIR studies (section 3.2.2) which suggested that MTMS is better hydrophobic agent than MTES and co-precursor method is more effective for synthesis of hydrophobic silica xerogels.

The behavior of hydrophilic and hydrophobic silica xerogels calcined at 400°C in ethanol and water adsorption as a function of specific surface area is shown in Figure 3-37. The highest hydrophobicity of sample synthesized by co-precursor method using MTMS as hydrophobic agent and calcined at 400°C (S2_400) is also evidenced. Differences in the adsorption capacities of hydrophobic silica xerogels prepared with MTES by co-precursor and derivatization method, (S5-400) and (S6-400) respectively, are observed. These are related with the higher specific surface area presented by the sample S5_400 in comparison with the others hydrophobic silica samples calcined at 400°C.

The highest hydrophobicity of the sample (S2_400) was also confirmed by adsorption studies of ethanol-water mixture (5 wt.% of ethanol, 95wt.% of water). This ethanol-water concentration was selected in accordance with ethanol removal concentration by pervaporation (5-10wt.%), an potential application of hydrophobic material. Figure 3-38 shows the selectivity toward ethanol of silica materials studied as adsorbents. Sample S2-400 presented the highest selectivity to ethanol adsorption (ca. 8).

On the other hand, the lowest hydrophobicity in the case of silica xerogels modified with MTMS and MTES by co-precursor method and calcined at 600°C and 750°C, respectively (samples S2_600 and S5_750) was observed. This is confirmed by the reduction in selectivity to ethanol adsorption (ca.3).

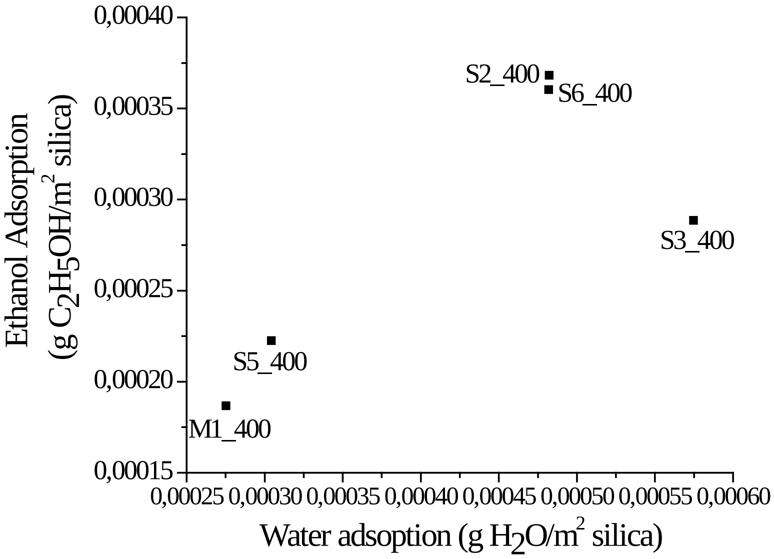


Figure 3-37. Ethanol and water adsorption capacity of hydrophilic and hydrophobic silica xerogels, units: g adsorbate / m^2 silica

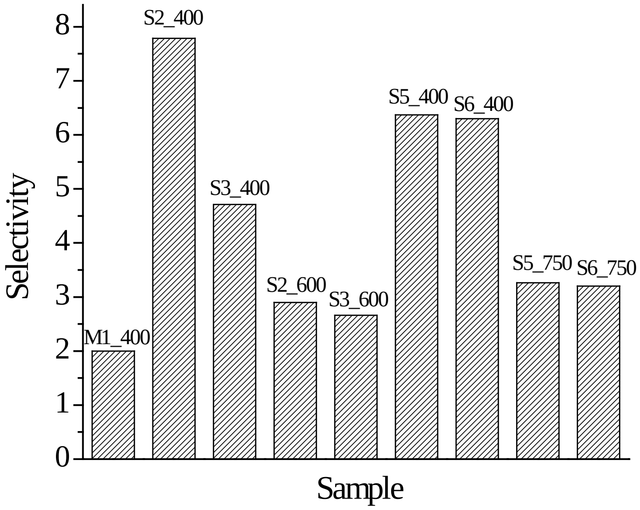


Figure 3-38. Selectivity toward ethanol in the adsorption of ethanol-water mixture (5 wt.% of ethanol, 95wt.% of water) on hydrophilic (M1) and hydrophobic material (S2,S3,S5 and S6) synthesized under different conditions.

Concluding, the co-precursor method gives some advantages in comparison with derivatization method. Co-precursor method offers a rapid surface modification of the gels. The addition of the surface modifying agent to the sol results in the surface as well as the bulk clusters modification, uniformly throughout the gel. Therefore, silica material modified by this method presents better hydrophobic properties .The derivatization method is tedious and time consuming since it involves the solvent exchange. The chemical modification using this method is only on silica surface; hence, less hydrophobic materials are obtained through derivatization method. Consequently, hydrophobic silica xerogel synthesized by co-precursor method using MTMS is selected as the most hydrophobic material obtained in this study. Potential application of hydrophobic silica xerogels will be presented.

3.2.5 Potential applications

3.2.5.1 Adsorption of alcohols

Chemical modification of silica can improve its application as adsorbent of organic compounds. Figure 3-39 shows the results of adsorption studies of pure alcohols: methanol, ethanol, butanol and pentanol, realized in the liquid phase, on hydrophobic silica xerogel synthesized by co-precursor method, using MTMS as hydrophobic agent. This material was selected for those studies basing on the results of previous analyses (section 3.2.4), taking as one of the criteria its adsorption capacity to ethanol.

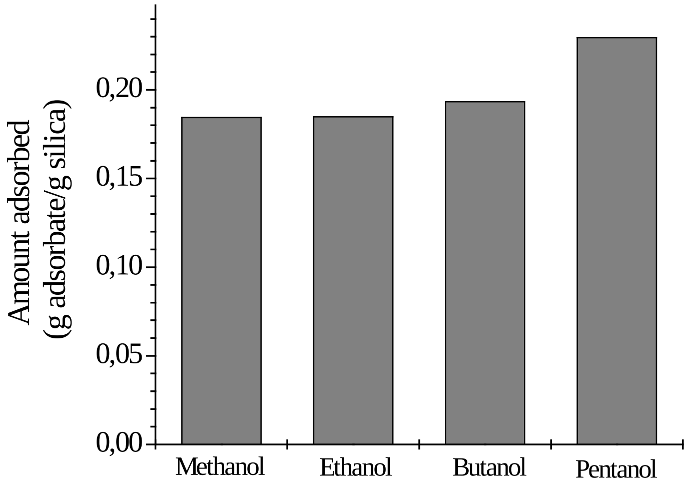


Figure 3-39. Alcohols adsorption on hydrophobic silica xerogel synthesized by co-precursor method using MTMS as hydrophobic agent and calcined

One can see that hydrophobic silica xerogels present higher (ca. 35%) alcohols adsorption capacity (Figure 3-39) than that of hydrophilic silica (Figure 3-14). The alcohols adsorption capacity increases in the following order: methanol < ethanol < butanol < pentanol. One can see that it is much higher for high molecular size adsorbates (butanol and pentanol). The observed behavior can be related to the surface tension of the studied adsorbates (Table 3-17). It could be seen that the increase in the liquid surface tension corresponds with the increase in adsorption capacity of the hydrophobic silica xerogel. This could be expected since surface tension and adsorption process are consequence of surface energy. High surface energy requires more energy to break down intermolecular bonds (Venkateswara Rao et al, 2007).

Table 3-17. Surface tension of adsorbates used in adsorption experiments (Lide, 2005)

Adsorbate	Surface tension (mN/m)
Methanol	22,45
Ethanol	22,38
n-Butanol	25,38
1-Pentanol	25,79

Once the adsorbate is absorbed, the mass of the liquid absorbed depends of the surface tension value of that liquid. In porous material, the absorption is due to the capillary action, therefore, capillarity force equation ($2\pi r cos\theta = mg$) is used. For the liquids that completely wet the surface of hydrophobic materials, the contact angle θ is approximately zero. Hence, for hydrophobic silica is valid the relation $\gamma = km$, between the amount of liquid adsorbed (m) and the surface tension (γ) (Venkateswara Rao et al., 2007).

The highest surface tension in the group of the studied alcohols is for pentanol (γ=25,79 mN/m), which is also adsorbed at higher amount by silica xerogel (0,2294 g pentanol /g silica). On the other hand, ethanol and methanol were adsorbed in similar quantities. It could be related to their similar molecular size (4,3Å and 4,1Å, for ethanol and methanol, respectively) and their equal superficial tension (≈22.4mN/m).

Concluding, the sequence of increasing adsorption capacity of the studied alcohols (methanol < ethanol < butanol < pentanol) was followed by the sequence of increasing surface tension and their molecular size. As far as we know, this kind of quantitative studies of alcohols adsorption over hydrophobic silica-based materials (not only xerogels) has not been reported in the literature so far.

3.2.5.2 Ethanol removal

A new application of hydrophobic silica xerogels in the field of membrane synthesis is proposed. As far as we know, this kind of material has not been applied before in the removal of organic compounds by pervaporation. Ethanol removal is an important step in ethanol production. Its concentration of 5-10 wt% is usually employed in ethanol-water separation. In this study, ethanol removal by pervaporation process was carried out using several hydrophobic silica membranes synthesized by co-precursor method using MTMS as hydrophobic agent, calcined at different temperatures.

The pervaporation performance of hydrophobic silica membranes for ethanol-water mixture (7wt.% ethanol) is presented in Figure 3-40(a). The observed decrease in total flux with the increase of calcination temperature can be related to the reduction of pore volume during thermal treatment, as confirmed by N_2-adsorption studies (section 3.2.3). On unsupported silica material this reduction is ca.17% between 400°C to 600°C.

Figure 3-40(b) presents ethanol selectivity and PSI factor of hydrophobic silica membranes, as function of calcination temperature. Ethanol selectivity and PSI factor clearly decreased while the calcination temperature increased. It could be related to the gradual loss of hydrophobic character of silica material, at calcination temperatures above 400°C, which was confirmed by TGA and FTIR studies in sections 3.2.1 and 3.2.2 respectively and the reduction of pore volume during the thermal treatment (section 3.2.3).

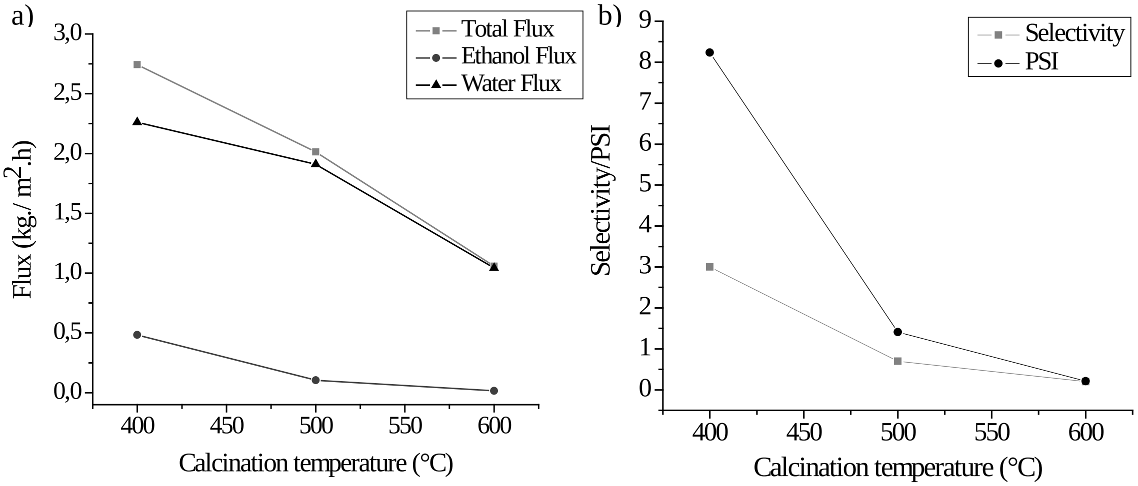


Figure 3-40. Pervaporation performance of hydrophobic silica membranes, calcined at different temperatures (water-ethanol mixture (7wt.% ethanol); pervaporation temperature 35°C)

The possible separation mechanism using hydrophobic silica membranes can be based on the combination of adsorption and diffusion effects (Bettens et al., 2006; Sommer & Melin, 2005). The solution–diffusion model is generally accepted as a good description of the mechanism of fluid transport, and is widely applied in the area of polymeric membrane research. However, applied to zeolite and ceramic membranes, it was renamed into the adsorption–diffusion model (Sekulic et al., 2005). Hydrophobic silica powders were characterized with pore size of 17Å, which is higher than the kinetic diameter of ethanol (4.4 Å) and water (2.8 Å) molecules. Therefore, it could be expected that both substances are able to diffuse through the membrane. Hydrophobic silica membrane calcined at 400°C, presented selectivity to ethanol in the separation process. Considering that it’s hydrophobic nature was already confirmed (sections 3.2.2 and 3.2.4), it could be expected that selective pass of ethanol through the membrane takes place. On the other hand, in the case of silica membranes calcined at higher temperature, the significant decrease in their selectivity was observed (Figure 3-40). This could be related to the observed changes in the hydrophobicity of material upon increasing temperature. As presented above (sections 3.2.1 and 3.2.2), the hydrophobic nature of the studied materials was conserved in air only up to ca. 570°C. According to the TGA-DTA-MS and FTIR studies (section 3.2.2), at temperatures above 570°C, the attached hydrophobic, methyl groups on silica surface were oxidized and material became hydrophilic again.

The adsorption studies of ethanol–water mixture (7wt.% ethanol, 93wt.% water) on hydrophobic silica powders (Figure 3-41) confirmed also the loss of ethanol adsorption capacity with an increases in the calcination temperature from 400 to 600°C (section 3.2.1 and 3.2.2).

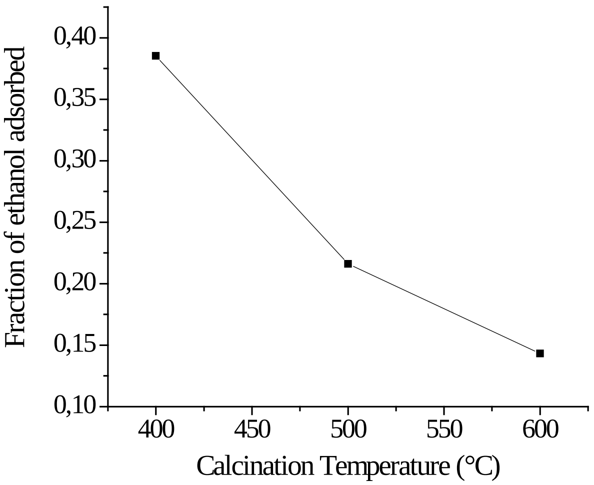


Figure 3-41. Adsorption of aqueous ethanol solution (7wt.% ethanol, 93wt.% water) on hydrophobic silica powders (sample S2)

Typically hydrophobic membranes used for ethanol removal by pervaporation are polymeric or zeolite-based (Vane, 2005). So far, ceramic membranes have not been used for this purpose. Selectivity of these membranes is reported in Table 3- 18. One can see that a zeolite-based as well as polymeric membrane presents higher selectivity to ethanol in comparison to hydrophobic silica membrane (this study). However it is difficult to compare pervaporation performance of those membranes due to the differences in material properties (pore size, surface area) and experimental conditions.

Table 3- 18. Separation selectivity of membranes used in ethanol removal by pervaporation

Membrane	Temperature (°C)	Selectivity	Ethanol Concentration (%)	Reference
PDMS	35	9	6	(Vane, 2005)
PTMSP	30	15	6	(Vane, 2005)
Silicalite-1	30	41	5	(Vane, 2005)
Hydrophobic silica	35	3	7	This study

PDMS: poly(dimethyl siloxane)
PTMSP :poly[1-(trimethylsilyl)-1-propyne]

Nevertheless, the scopes of this research lead to select the synthesized method, the type of hydrophobic agent to synthesize hydrophobic silica membranes, their calcination temperature. Co-precursor method and MTMS were established as better preparation method and hydrophobic agents, respectively.

Basing on those studies, it was possible to determine the relations between adsorption capacity of the studied materials, influenced by their physico-chemical properties, and its performance in the pervaporation process. Higher capacity of xerogel in ethanol adsorption in the liquid phase was followed by its better performance in pervaporation process. These are important point; taking into consideration the quite complicated and time consuming process of ceramic membrane preparation. It could be suggested that basing on the adsorption results realized in the liquid phase, the general prediction of membrane performance in pervaporation process can be made.

3.2.6 Conclusions

- The significant effect of the preparation method, the type of the hydrophobic agent and the calcination temperature on the surface, textural and morphological properties of hydrophobic silica xerogel were observed. Microporous and amorphous material is obtained by synthesis of hydrophobic silica with MTMS by co-precursor and derivatization methods and by derivatization method with MTES. Mesoporous material is obtained using the co-precursor method with MTES.

- Chemical modification of silica xerogels was confirmed by FTIR and ethanol adsorption studies. The additional interaction bands at 1279 and 840cm^{-1} related to the Si-C stretching vibrations, observed on modified samples, ratified the attachment of methyl groups to silica network and its surface during chemical modification. Higher ethanol adsorption capacity was also observed for modified silica in comparison to the hydrophilic silica. Therefore chemical modification of silica surface gave hydrophobic features to silica xerogels.

- Silica xerogel prepared by co-precursor method, using MTMS presented the highest ethanol adsorption capacity (0,1848 g ethanol/g silica). Taking it as the criterion, co-precursor method and MTMS hydrophobic agent are considered as more effective for hydrophobic xerogels synthesis.

- Silica xerogels modified with MTES retains their hydrophobicity up to 590°C in air atmosphere ; meanwhile, the material modified with MTMS loss the hydrophobic properties above 570°C .

- Silica xerogels prepared using MTMS and MTES as hydrophobic agents and calcined at 600°C and 750°C presented the lowest ethanol adsorption capacities. This is attributed to the loss of hydrophobicity during the thermal treatment at temperatures higher than 500°C.

- The alcohols adsorption capacity increases in the following order: methanol < ethanol < butanol < pentanol. The sequence of increasing adsorption capacity followed the sequence of increasing surface tension and molecular weight of the adsorbate.

- As far as we known, no similar research (quantitative) has been reported over the application of hydrophobic silica xerogels as alcohol adsorbent material and hydrophobic ceramic material.

- Pervaporation performance of hydrophobic silica membranes in ethanol removal depends on its calcination temperature. Better flux and ethanol selectivity were obtained with silica membranes calcined at 400°C, temperature in which hydrophobicity is retained.

- The determination of the relation between adsorption capacity of the studied materials, influenced by their physico-chemical properties, and its performance in the pervaporation process was established. Higher capacity of xerogel in ethanol adsorption in the liquid phase was followed by its better performance in pervaporation process. This is important point; taking into consideration quite complicated and time consuming process of ceramic membrane preparation. It could be suggested that basing on the adsorption results realized in the liquid phase, the general prediction of membrane performance in pervaporation process can be made.

Chapter 4.
General conclusions and future perspectives

4.1 General conclusions

Silica xerogels have been considered as exceptional material with numerous applications in science and engineering. Nevertheless the hydrophilic nature of silica limits their applications. The material can be deteriorated by water adsorption via hydrogen bonding between water molecules and silanol groups presented on silica surface. The replacement of the H from the surface hydroxyl groups (Si–OH) with the hydrolytically stable alkyl or aryl groups (Si–R), through the oxygen bonds, can prevent the adsorption of water and hence results in hydrophobic silica surfaces.

Therefore, the aim of this thesis was to gain a more detailed insight into the different factors controlling the adsorptive properties of silica-derived xerogels. The influence of the physico-chemical properties on their performance as adsorbents of organic compounds (alcohols) and as materials for preparation of inorganic membranes for ethanol removal and purification has been studied.

The findings addressed in this thesis can, in general, be divided into two related subjects: *i.* hydrophilic silica characterization and its potential applications and *ii.* hydrophobic silica characterization and its potential applications.

i. Hydrophilic silica characterization and its potential applications

- Hydrophilic silica xerogels synthesized by sol-gel method using the standard molar ratio TEOS (1): ethanol (3.8): water (6.4): nitric acid (0.085) are microporous materials (pore width 17Å) with large specific surface area (> 500 $m^2.g^{-1}$).

- The aging time have significant effect on the morphological properties of hydrophilic silica xerogels. Longer aged periods cause strength of silica network reducing the shrinkage during the thermal treatment.

- Hydrophilic silica xerogel properties depend strongly on calcination temperature. Calcination process causes the densification of silica network by condensations reactions. The reduction of micropore surface and volume and the change in morphology during calcination are a strong indication of that effect. The minimum calcination temperature of hydrophilic silica xerogel was established as 400°C in air atmosphere.

- Microporous hydrophilic silica membranes are promising material for alcohols dehydrations. The selectivity to water obtained for ethanol-water (6wt % water in ethanol) separation by pervaporation was 207. This selectivity value has been one of the highest reported in the literature for ethanol dehydration.

- The dip-coating velocity and membrane calcination temperature have significant influence on the pervaporation performance of silica membranes. The highest pervaporation separation index was obtained for hydrophilic silica membranes deposited at 1cm.s^{-1} and calcined at 400°C.

ii. Hydrophobic silica characterization and potential applications

- Hydrophobic silica xerogels were synthesized successfully by the modification methods proposed for silica aerogels: co-precursor and derivatization, using MTMS and MTES as hydrophobic agents.

- The attachment of methyl groups from MTMS and MTES to silica xerogels conferred hydrophobic properties, increasing the alcohols adsorption capacity of those materials.

- Ethanol adsorption studies in liquid and gas phase and FTIR measurements suggest that MTMS is better hydrophobic agent than MTES and that the co-precursor method is more effective preparation method than derivatization one.

- Adsorption properties of hydrophobic silica xerogel was found to be dependent on calcination temperature and related to hydrophobic properties. The thermal stability in air atmosphere of hydrophobic silica xerogels was established up to 570°C and 590°C for material synthesized using MTMS and MTES, respectively

- As far as we known, no similar research (quantitative) has been reported over the application of hydrophobic silica xerogels as alcohol adsorbent material and hydrophobic ceramic membranes.

- The alcohols adsorption capacity was increasing in the following order: methanol < ethanol < butanol < pentanol. The sequence of increasing adsorption capacity is followed by the sequence of increasing surface tension and molecular weight of the adsorbate.

- Pervaporation performance of hydrophobic silica membranes in ethanol removal depends on calcination temperature. Better flux and ethanol selectivity were obtained for silica membranes calcined at 400°C, temperature which hydrophobicity is reteined.

4.2 Future perspectives

In this thesis the potential applications of silica xerogels as alcohols adsorbent materials and membranes for ethanol removal and ethanol purification were exposed.

The increasing interest in bio-ethanol production and the application of hydrophobic silica membranes for ethanol removal and hydrophilic silica membranes for ethanol dehydration by pervaporation can potentiate this process from energetic and environmental point of view.

In order to improve the performance of synthesized hydrophobic silica membranes in pervaporation process, the following aspects for future studies can be considered:

- application of different TEOS : hydrophobic agent molar ratios for xerogels synthesis
- application of hydrophobic agent with different than methyl functional groups

Moreover, considering that alcohol adsorption capacity significantly depends on the surface tension and molecular size of the adsorbate, the application of prepared membranes in the separation of other water-alcohol mixtures can be considered (e.g. butanol, as possible alternative fuel).

Annex 1
Contributions related to this thesis

The following contributions were prepared during this thesis:

- **A.C. Duque Salazar**, I. Dobrosz-Gómez, M.A. Gómez-García , J. Fontalvo, M. Jedrzejczyk, J.M. Rynkowski. “Chemical modification of silica xerogels for the adsorption of organic compounds”. To be submitted to Sol-Gel Science and Technology.
- **A. C. Duque Salazar,** J. Fontalvo, M. A. Gómez-García, I. Dobrosz-Gómez. “Membranas cerámicas microporosas a base de sílice para la producción de etanol”; accepted to XXVI Congreso de Ingeniería Química "Energía y desarrollo regional sostenible". Barrancabermeja-Colombia, 2011.
- **A.C. Duque Salazar,** M.A. Gómez García, J. Fontalvo, M. Jedrzejczyk, J.M. Rynkowski, I. Dobrosz-Gómez.“Removal and purification of ethanol by pervaporation using microporous silica membranes“; accepted to International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation”. Torun-Poland, 2011.

Some additional contributions were developed during the scientific stage in Technical University of Lodz, Poland:

- I. Dobrosz-Gómez, **A.C. Duque Salazar**, M.A. Gómez García, J. Bojarska, M. Jedrzejczyk, J.M. Rynkowski. “Nanocrystalline zirconia powders via aqueous combustion synthesis”; accepted to X EuropaCat. Glasgow-Scotland, 2011.
- J. Bojarska, I. Dobrosz-Gómez, **A.C. Duque Salazar**, M.A. Gómez García. J. Fontalvo Alzate. J.M. Rynkowski. “Combustion synthesis and x-ray phase analysis of nanocrystalline ZrO_2”; 52 Konwersatorium krystalograficzne (Polish Crystallographic Meeting. Wroclaw Poland. June 24-26 – 2010.
- I. Dobrosz-Gómez, **A.C. Duque Salazar**, M.A. Gómez García, J. Bojarska, M. Jedrzejczyk, J.M. Rynkowski. “Combustion synthesis and physico-chemical properties of nanocrystalline ZrO_2 powder”. In preparation

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