Sándor Mónika

Synthesis of Silica Particles Grafted with Organic Groups

- PhD Thesis Summary -

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Contents

Keywords: *sol-gel process, hybrid silicas with modified surfaces, humic acids immobilization, polyether polyol, activated silica supports*

Acknowledgments

Note: *The original numbering of figures and tables from the thesis has been preserved throughout this summary.*

List of abbreviations

AHA   humic acids from Aldrich

APTES   (3-aminopropyl)triethoxysilane

BATMS   bis[3-(trimethoxisilyl)propyl]amine

BETES   1,2-bis(triethoxysilyl)ethane

BETMS   1,2 bis(trimethoxysilyl)ethane

DABCO   1,4-diazobicyclo(2.2.2)octane

FIN   benzoinedimethylacetal

GPTMS   (3-glycidyloxypropyl)trimethoxysilane

HA   humic acids

HS   humic substances

Me_2DES diethoxydimethylsilane

Me_3ES trimethylethoxysilane

Me_3MS methoxytrimethylsilane

MeTES   methyltriethoxysilane

MeTMS   methyltrimethoxysilane

NCOTEOS   (3-isocyanatopropyl)triethoxysilane

OOT   onset oxidation temperature

PEO   polyether polyol type PETOL-36-3 BR

PHA   humic acids extracted from peat

PPO   polyether polyol type PETOL-48-3 MB

TEOS   tetraethyl orthosilicate

TIP   tetraisopropylorthotitanate

VTES   triethoxyvinylsilane

Introduction

The sol-gel method is a multidisciplinary approach, which has allowed the emergence of highly complex materials with various and new functionalities. This can be used in a wide range industrial sectors and applications in various fields (catalysts, sensors, active optical component and transparent materials, etc.).

Sol-gel preparation method confers special properties to the final material, including: porosity, high homogeneity, high pore volume, very low density and large specific surface area [1].

Silica particles can be obtained by hydrolysis and condensation of precursors, e.g., metal alkoxides, according to the sol-gel process. Silica based organic-inorganic hybrid materials can be prepared by modification of the surface silanol functions. The active hydrogen atoms of the silanol groups dispersed on a silica particle surface can react with organosilyl groups of the general formula $(RO)_3SiY$, with Y being an organic chain containing the required functional groups [2].

The method facilitates preparation of silica hybrid particles functionalized with groups (e.g., amino or glycidyloxy functions), which are capable to interact with humic acids. During the synthesis – beside these coupling agents – can be grafted on the silica surface mono-, bi- and trifunctional derivatives to block some surface residual Si-OH groups, thus allowing an easier access for humic acids to coupling agents.

The humic acids are macromolecular, heterocyclic, condensed substances, with different degree of polymerization and multiple, complex organic functions [3]. The humic acid activated support ought to combine insolubility, the mechanical, thermal and chemical stability and porosity of the silicate matrix with the biosorption capacity of humic acids [4].

Humic acid-silica supports can be used as a bioabsorbent because have been shown to be effective for reducing of inorganic or organic pollutants from wastewater or from other solvents [5-8], while avoiding humic acid loss by solubilization; for enzyme immobilization [9]; and for investigations of the binding properties of radio nuclides and organic pollutants to soil and sediment [2]. In addition, another advantage is that these hybrid materials can be reused without creating waste [10].

One of the main advantages of bioabsorbent is very abundant in the nature with a low cost (compared to the synthetic adsorbent), it is very effective and non-toxic [11].

The coupling of different organic substances with silica hybrid particles results a material with improved properties. Hybrid materials grafted with organic polymers are more flexible and less susceptible to cracking during the drying stage [12-13], and the same time the inorganic component provides a high thermal stability [14,15].

Purpose and objective of the thesis

The **GENERAL PURPOSE** of this study is to obtain new nanomaterials based on silica hybrid particles which are capable to interact with organic substances.

The **FIRST OBJECTIVE** of the doctoral thesis is synthesis and characterization of silica hybrid materials, synthesized in the presence of silica co-precursors, grafted with functional groups capable of interacting with humic acids.

The **SECOND OBJECTIVE** is focused on the functionalization of the amino or glycidyloxy grafted silica particles with humic acids.

To achieve the first two objectives, we need to make thorough theoretical and experimental studies on:
− extraction of peat humic acids from Comandău;
− obtaining silica particles using base catalyzed sol-gel method;
− generating amino or glycidyloxy functions (in some cases simultaneously alkyl groups) onto preformed silica particles;
− grafting humic acid macromolecules on the surface of the silica hybrid particles;
− assessment of physicochemical properties of synthesized materials depending on the working parameters.

The **THIRD OBJECTIVE** of the study is to obtain and characterize of silica hybrid materials, synthesized in the presence of polyether polyols as such or functionalized with (3-isocyanatopropyl)triethoxysilane.

To achieve the third objective, we conducted a theoretical and experimental research on:
− initial functionalization of polyether polyols with (3-isocyanatopropyl)triethoxysilane;
− obtaining different silica particles grafted with polyether polyols as such or modified with NCOTEOS, in acid catalyzed sol-gel reaction;

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– evaluating the coupling degree of polyether polyols and investigating the stability of the obtained materials by various methods.

PhD thesis structure

This thesis is organized in seven main parts including an introductory section, data from the literature, personal researches and results and finishes with general conclusions.

The introductory section generally describes the importance of the sol-gel method, how to obtain silica hybrid particles from alkoxide silanes, the possibility of grafting humic acids or polyether polyols to the silica surface resulting hybrid materials with advanced properties and their importance. It also presents the purpose and objectives of this research.

The first part contains a literature review about sol-gel process, methods for preparation and surface modification of silica particles and describes interactions of hybrid materials with humic acids and polyether polyols.

The second part of this thesis relates to the preparation and characterization of silica hybrid particles synthesized by base catalyzed sol-gel method in aqueous medium, using various coupling agents (amino or glycidyloxy groups) and spacers (alkyl groups).

The third part shows the humic acids coupling efficiency of the synthetized silica hybrid particles functionalized with amino or glycidyloxy groups (in some cases the coupling agents are spaced by alkyl groups). This section focuses on the interactions between the organically grafted silica hybrids and two types of humic acid.

In the last part, we studied the possibility of obtaining various silica hybrid materials, synthesized in the presence of two commercially available polyether polyols – as such or functionalized with (3-isocyanatopropyl)triethoxysilane (NCOTEOS) – produced in situ by acid catalyzed sol-gel technique. Evaluation of the coupling degree of the polyols to the silica network and the stability of the obtained materials characterized by different methods were also detailed.

Finally, the main conclusions are summarized and followed by references and annexes of the thesis.

Chapter 1. Theoretical aspects

Silica nanoparticles occupy a prominent position in scientific research because of their easy preparation and are widely used for various multidisciplinary applications in different areas. Therefore, in recent decades, intensive worldwide research has been achieved in order to identify new methods and detect and extend the application fields of the silica based materials.

Metal alkoxides represent the class of precursors, which are most extensively used in the sol-gel research. Hydrolysis and condensation of such precursors lead to the formation of the silica particles [16,17]. Hydrolysis and condensation reactions are influenced by several factors such as pH, temperature, chemical nature of the alkoxy groups and solvent. Among these factors, the pH plays an important role because it is known that in an acid catalyzed sol-gel reaction, the hydrolysis is much faster than the condensation. This leads to a three-dimensional network that contains residual silanol groups which can interact through hydrogen bonds. Due to these interactions, the condensation degree is not very high. Otherwise, in a base or organometallic catalyzed sol-gel reaction, the hydrolysis is very slow. The resulting three-dimensional network does not contain residual silanol groups and the condensation degree is much higher.

Silica based nanoparticles have an important role in the modern materials science. After the formation of the silica particles, the silanol groups from the silica surface can be easily modified by various physical and/or chemical techniques, thus changing the physicochemical properties of the formed colloidal system, for example hydrophobization of the particle which had initial a hydrophilic character.

In the case of sol–gel materials hybrid silicas can be obtained from the hydrolysis and co-condensation of tetraethyl orthosilicate (TEOS) with other organosiloxanes ($R_xSi(OR)_{4-x}$, where R is an alkyl group). In these materials, TEOS functions – as building blocks – construct the framework while the organosiloxanes with non-hydrolysable organic groups contribute both to the framework silica units and to organic surface functional groups.

Therefore, during the sol-gel process tetrafunctional organosilanes can be used together with mono-, di- and trifunctional organoalkoxysilanes having one, two or three nonhydrolysable groups which can be reactive, acting as a coupling agent (amine [18] or isocyanate [19]) or unreactive (alkyl groups) having a spacing role [20].

The formed organic-inorganic hybrid materials are extensively studied in the literature [10,16]. These hybrid materials combine the properties of inorganic (e.g., low density, heat resistance, retention of mechanical properties at high temperature and low thermal expansion) and organic compounds (e.g., flexibility, low dielectric constant and ductility) in one material [10,21].

Organosilane compounds may be used for modifying and improving the silica surface's properties. The surface structure of the silica particles can be changed depending on the reaction conditions [11,20,22], hybrid material contains the desired functional groups on its surface.

One of the most promising applications of the hybrid materials is their usage as a support to immobilize biomolecules, especially humic acids. The preparation of hybrids functionalized with humic acids leads to the formation of new materials with complexation characteristics of humic acids and with the insolubility, thermal and chemical stability characteristics of the silica [4].

Incorporation of organic polymers in an inorganic silica framework is also possible; it makes the final material more flexible and less susceptible to cracking during the drying stage [12,13], with a high thermal stability characteristic of the inorganic component [14].

Chapter II. Preparation of silica particles functionalized with amino groups

II.1 Synthesis of silica supports with amino functions

A method adapted from references [23,24] was used for the synthesis of the amino-functionalized silica particles, through a two-step sol-gel method:

Step 1. Preparation of pristine silica particles (preformed SiO_2 particles): 40 mL of ammonia and 200 mL of ethanol were introduced in a flask equipped with a mechanical stirrer, condenser and addition funnel. 10 g (0.048 moles) of TEOS diluted in 40 mL of ethanol were rapidly added to this mixture and kept under stirring (~ 200 rpm) for another two hours at room temperature.

Step 2. Preparation of amino-functionalized silica particles (NH_2-SiO_2 particles): over the dispersion prepared in Step 1.0532 g of APTES (0.0024 moles) diluted in 4 mL ethanol were continuously added for two hours. This amount represents an APTES/TEOS molar ratio of 1/20 according to the method described by Brambilla et al. [24].

In some cases, the alkyl derivatives (spacers for the amino functions) were added together with APTES to the reaction system. The final mixture was further stirred for two more hours and then allowed to rest overnight. Subsequently, one part from the resulted dispersion was kept in a closed bottle and another part has been transferred to a Petri dish and allowed to dry at room temperature for 3–4 days. Finally it was dried under vacuum at 40 °C.

For preparation of **sample 1** (only APTES), 10.6 g APTES diluted in 40 mL EtOH were introduced over a mixture of 40 mL NH_4OH 25% and 200 mL EtOH. The reaction was kept under stirring for four hours and left overnight. The next day the whole mixture was a homogenous and transparent dispersion. After the removal of the volatile compounds, the resulted solid was transparent and difficult to be milled. This reference sample was prepared in order to demonstrate the effect of steric hindrance over the ability to immobilize the HA, as a result of the high density of the amino groups.

All silica particles synthetized in the presence of 3-aminopropyltriethoxysilane and the used molar ratios are listed in **Table 2.1**.

II.2 Characterization techniques

The structure and morphology of silica particles were characterized using different techniques:

- elemental composition – *Elemental Analysis (**C,H,N**)*;
- thermal behavior – *Thermogravimetric Analysis (**TGA**)*;
- average hydrodynamic diameter and particle size distribution – *Dynamic Light Scattering (**DLS**) Technique*;
- zeta potential – *Laser Doppler Velocimetry (**LDV**) Technique*;
- morphology – *Environmental Scanning Electron Microscopy (**ESEM**)*;
- structure – *Fourier Transformed Infrared Spectroscopy (**FTIR**) and Solid State Nuclear Magnetic Resonance (**ssNMR**)*.

II.3 Results and discussions

II.3.1 Elemental Analysis (C,H,N)

Table. 2.1 *Contents of carbon, nitrogen and hydrogen for the different silica systems*

Sample no.	Silica system	Molar ratio	Carbon (%)	Nitrogen (%)	Hydrogen (%)
1	APTES	-	27.63	9.64	6.13
2	TEOS	-	0.94	0.55	1.36
3	TEOS/APTES	20/1	5.98	2.30	2.15
4	TEOS/APTES/MeTES	20/1/1	3.27	1.21	1.87
5	TEOS/APTES/Me$_2$DES	20/1/1	4.74	1.61	2.25
6	TEOS/APTES/Me$_3$ES	20/1/1	3.83	1.58	1.89
7	TEOS/APTES/BETES	20/1/0.5	4.42	1.57	2.06
8	TEOS/APTES/Me$_3$ES	10/1/1	5.01	1.86	1.72
9	TEOS/BETES	10/0.5	2.96	0	1.49
10	TEOS/Me$_3$ES	10/1	2.15	0.77	1.42
11	TEOS/Me$_2$DES	10/1	3.02	0	1.41
12	TEOS/BAPTMS	2/1	19.76	4.64	4.39

The carbon percentage contents are listed in **Table 2.1** and vary according to the precursor's molar ratio used in the sol-gel process. Obviously, the highest carbon content was

measured for silica particles synthesized only from APTES (**sample 1**), while the lowest for the particles containing only TEOS in the sol-gel mixture (**sample 2**), Grafting of APTES on the preformed SiO_2 particles (**sample 3**) increases the carbon weight share in the final hybrid.

For samples in which, besides TEOS and APTES, alkyl-derivatives were also added to the sol-gel reaction mixture (**samples 4-8**), the carbon content is slightly lower than the recorded value of the TEOS/APTES system.

II.3.2 Thermogravimetric Analysis (TGA)

The TGA results were consistent with previously presented data; the weight loss being in general proportional to the carbon content, the observed small deviations being caused by the removal of the adsorbed water in the first temperature range.
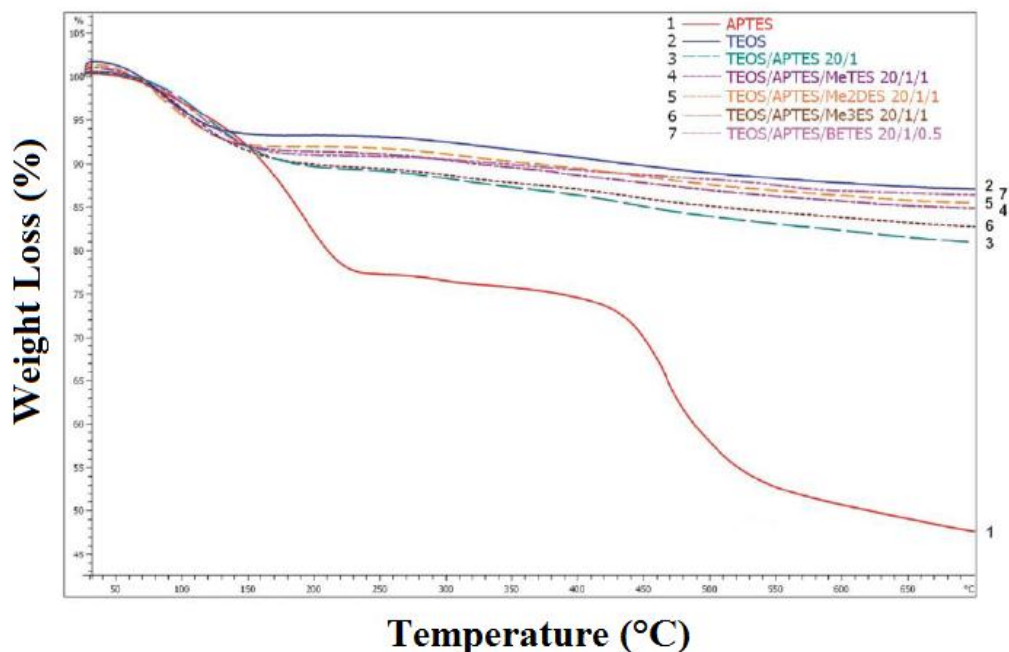
Figure 2.4 *Thermogravimetric (TG) curves of aminopropyl-silica particles*

Sample 1 (only APTES particles), with the highest carbon content, showed the highest value of weight loss, while for **sample 2** (only TEOS particles), having the lowest carbon content, was showed the lowest value of the weight loss.

Figure 2.4 shows the TG profiles of different aminopropyl functionalized silica systems. The most important differences were observed in the first temperature range (25-250 °C), which

corresponds to the release of water and other solvents. Having a hydrophilic character and a less cross-linked network, **sample 1** shows the highest weight loss due to water removal.

The second temperature range (250-450 °C) was due to the degradation of aminopropyl and of alkyl chains (when alkyl silanes were added to the sol-gel system). The third temperature range (450-700 °C) corresponds to dehydroxylation of Si-OH residual functions, which led to the formation of Si-O-Si groups. **Sample 1** (only APTES), which has a bulky aspect after drying, exhibits a larger weight loss due to the higher content of uncondensed Si-OH functions.

Table 2.2 The values of weight loss and related inorganic residue measured at 700 °C

Sample no.	Silica system	Molar ratio	Weight Loss (%)			Inorganic residue at 700°C (%)
			25-250 °C	250-450 °C	450-700 °C	
1	APTES	-	23.1	7.5	22.1	47.3
2	TEOS	-	9.6	2.3	2.3	85.8
3	TEOS/APTES	20/1	11.0	4.4	4.1	80.5
4	TEOS/APTES/MeTES	20/1/1	9.6	3.7	2.9	83.8
5	TEOS/APTES/Me$_2$DES	20/1/1	9.4	3.5	3.0	84.1
6	TEOS/APTES/Me$_3$ES	20/1/1	11.0	3.6	3.2	82.2
7	TEOS/APTES/BETES	20/1/0.5	8.5	3.5	2.7	85.3
8	TEOS/APTES/Me$_3$ES	10/1/1	13.6	4.6	5.1	76.7
9	TEOS/BETES	10/0.5	10.6	4.1	2.2	83.1
10	TEOS/Me$_3$ES	10/1	8.9	4.2	1.6	85.3
11	TEOS/Me$_2$DES	10/1	11.6	3.8	2.1	82.5
12	TEOS/BAPTMS	2/1	18.0	14.7	5.1	62.2

The value of the inorganic residue measured at 700 °C decreased accordingly to the increase in the content of organic compounds (**Table 2.2**).

II.3.3 Particle size measurements (Dynamic Light Scattering (DLS) Technique)

In **Table 2.3** are presented the values of the average hydrodynamic diameters recorded for samples diluted in distilled water. For **sample 1**, the measured average particle diameter is 580 nm. The measurement precision for this sample was lower because the sol dispersion was very complex, containing aggregates of various sizes. After drying of this sol-gel system a bulky

material was obtained. **Sample 2** has an average diameter of 549 nm and a narrow size distribution, indicating the successful synthesis of uniform Stöber silica particles.

Table 2.3 *Particle size and zeta potential values for the studied supports*

Sample no.	Silica system	Molar ratio	Average Diameter (nm)	Zeta Potential (mV)
1	APTES	-	580	-19
2	TEOS	-	549	-45
3	TEOS/APTES	20/1	691	15
4	TEOS/APTES/MeTES	20/1/1	1471	52
5	TEOS/APTES/Me$_2$DES	20/1/1	858	27
6	TEOS/APTES/Me$_3$ES	20/1/1	653	13
7	TEOS/APTES/BETES	20/1/0.5	716	53
8	TEOS/APTES/Me$_3$ES	10/1/1	558	-5
9	TEOS/BETES	10/0.5	590	-48
10	TEOS/Me$_3$ES	10/1	613	-54
11	TEOS/Me$_2$DES	10/1	633	-40
12	TEOS/BAPTMS	2/1	630	35

According to the DLS measurements, by grafting the aminopropyl functions on the surface of preformed silica particles, the hydrodynamic diameter of the resulted particles increases from 549 (**sample 2**) to 691 nm (**sample 3).** When alkyl derivatives have been used, the particles size depends on the addition of alkyl-silanes beside APTES in the reaction system.

When BETES is used as spacer (**sample 7**), the recorded average diameter (716 nm) is just slightly higher than the one recorded for **sample 3** (691 nm). Though, a narrower size distribution is shown for **sample 7** compared with **sample 3**, being already well known that BETES acts as a cross-linking agent in the sol-gel reaction, leading to a more compact silica network (**Figure 2.5**). It also should be noted that, by introduction of the methyl or dimethyl spacers, the size increases significantly and the distribution becomes much broader. This is probably due to the increased ability of particles to form aggregates due to the hydrophobic interaction induced by the methyl groups (**Figure 2.5**). Therefore, the highest values of the average hydrodynamic diameter (**Table 2.3**) were registered for **samples 4** (1471 nm) and **5** (858 nm), respectively. These two samples showed a very hydrophobic behavior, floating on the top

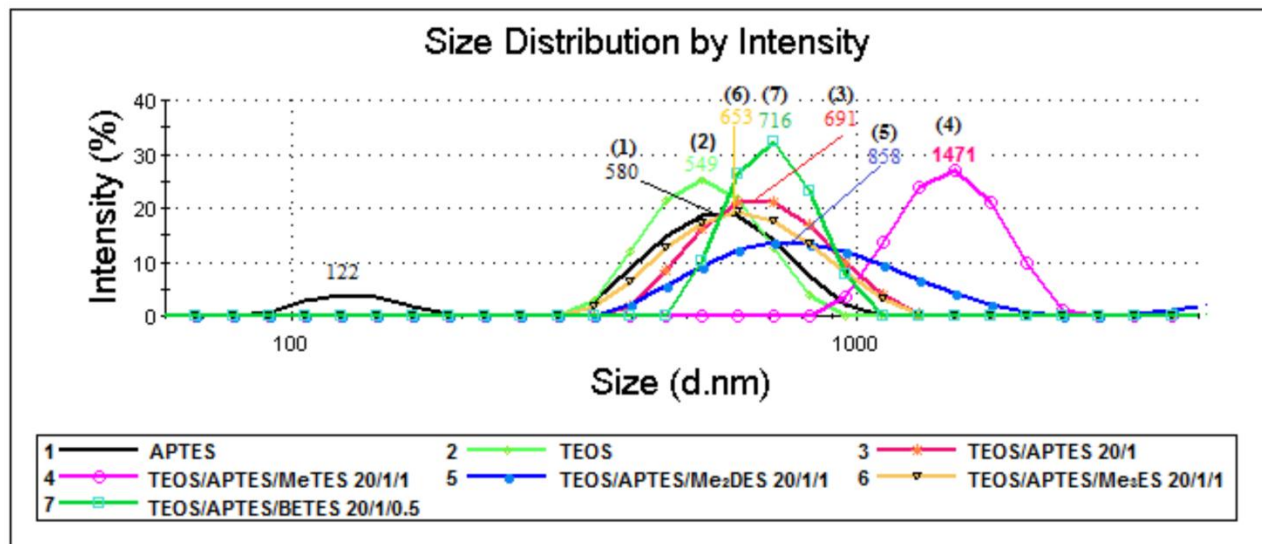of the aqueous dispersion and requiring an increased effort to be homogenized for the DLS measurement.

Figure 2.5 *Size distributions by intensity of aminopropyl silica particles*

A surprising result was obtained for **sample 6** (where Me_3ES has been used as a spacer); the average diameter (653 nm) and size distribution were almost similar to that obtained for **sample 3** (691 nm), indicating the absence of integration of the trimethyl derivative in the formed silica network.

II.3.4 Zeta potential measurements (Laser Doppler Velocimetry (LDV) Technique)

In **Figure 2.6**, zeta potential values (the potential that exists at the particle's hydrodynamic share or slipping plane boundary) are illustrated for samples dispersed in distilled water. As we expected, for **samples 2** and **9**, the value of zeta potential is highly negative (-45 mV and -48 mV, respectively), due to the high density of residual Si-OH present on the surface of silica particles.

By grafting the aminopropyl functions onto the surface of the preformed silica particle, the surface charge of particles was modified. As a result, the value of zeta potential shifts towards positive values (**samples 3-7**, **Table 2.3**). In addition, the alkyl-aminopropyl hybrids (**samples 4-7**) show an increase of zeta potential values, with the increase of the probability of interaction of the Si-OH from the particles surface with the available reactive ethoxy groups from the alkyl-silanes. In these conditions, in distilled water, the $-NH_2$ functions from APTES

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can be protonated in an increasingly higher extent. Thus, co-grafting (beside APTES) of di- or trifunctional alkyl-silanes (MeTES - **sample 4** and BETES - **sample 7**) led to the highest values of zeta potential (52 and 53 mV, respectively).

The hybrid with the bifunctional co-precursor (Me$_2$DES - **sample 5**) exhibited a lower zeta potential (27 mV), while the use of the monofunctional co-precursor (Me$_3$ES - **sample 6**) led to a value of zeta potential (13 mV) very similar with the one recorded for the hybrid prepared from APTES and TEOS (**sample 3**, 15 mV).
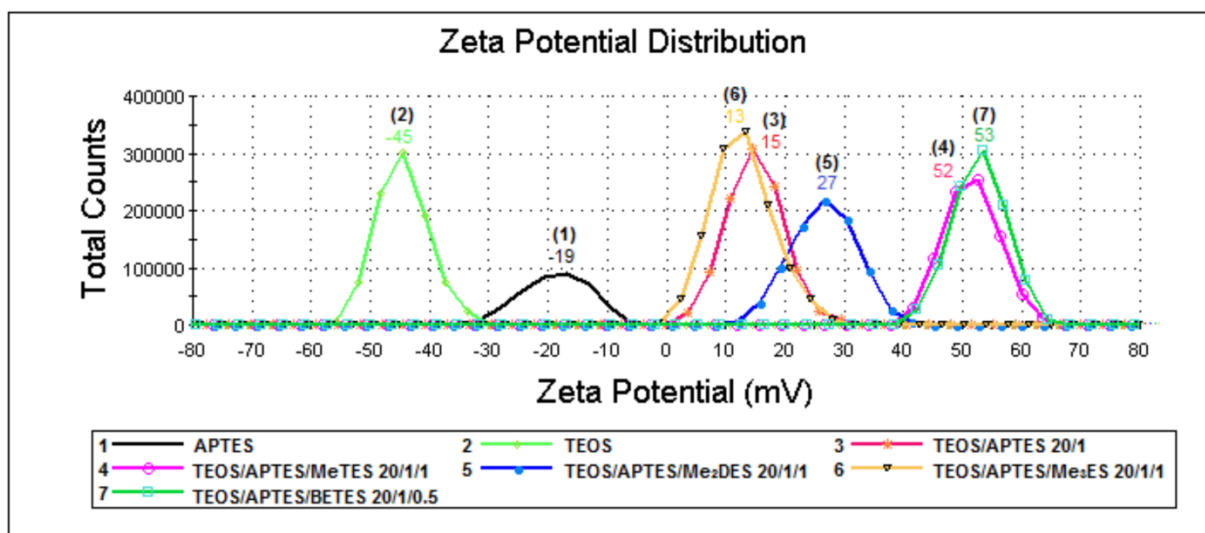
Figure 2.6 *Zeta potential distributions of aminopropyl silica particles*

For **samples 1** and **8**, by significantly increasing the aminopropyl density, these hydrophobic chains tend to self-associate and to orientate towards the interior of silica particles. A phase-inversion mechanism occurs, the -NH$_2$ functions being mostly hidden inside the silica hybrid frame, while towards water remain predominantly exposed Si-O charges. Thus, for the both samples, the value of zeta potential remains negative (-19 mV and -5 mV, respectively), but less negative than the one recorded for samples without APTES, since the amino functions are still partially able to interact with the surrounding medium.

II.3.5 Environmental Scanning Electron Microscopy (ESEM)

ESEM images of some of the studied aminosilica hybrids are shown in **Figure 2.7**. **Sample 1**, obtained from the sol-gel reaction of APTES precursor, is a film forming hybrid, of which cross-section can be seen in **Figure 2.7a**. In **Figure 2.7b**, the uniform and spherically

shaped SiO$_2$ particles resulted from the TEOS precursor (**sample 2**) are clearly shown. By grafting a small amount of APTES on these preformed SiO$_2$ particles (1 mole of APTES at 20 moles of TEOS), no significant change in the particles shape or size could be seen (**Figure 2.7c**).
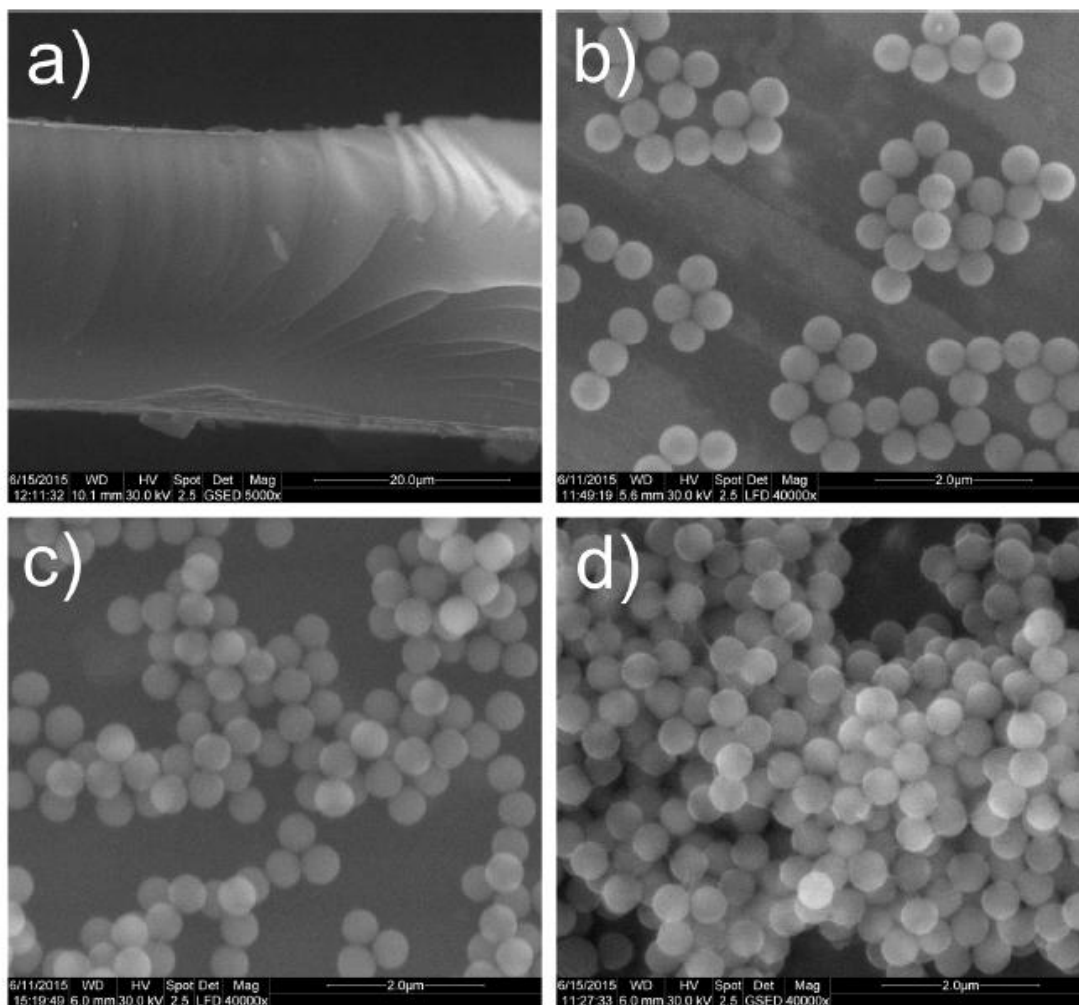
Figure 2.7 *ESEM images of: (a) APTES film (sample 1); (b) pristine TEOS silica particles (sample 2); (c) APTES -grafted silica particles (sample 3); and (d) MeTES and APTES -grafted silica particles (sample 4)*

The particles size estimated by ESEM analysis seems to not change after grafting the aminopropyl or alkyl chains onto particle's surface. Thus, for **sample 4** (**Figure 2.7d**), a closer packing of the methyl- and aminopropyl-functionalized particles is noticed due to the hydrophobic interactions. However, the size of the individual particles seems unchanged after drying.

II.3.6 Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 2.8 shows the FTIR spectra in the region 4000-400 cm^{-1} of the pristine silicas (**samples 1** and **2**) and of aminopropyl-grafted silica hybrids (**samples 3-7**). Because APTES used for functionalization of the silica particles have a very small weight share compared with TEOS used to obtain the initial particles (TEOS/APTES = 20/1 molar ratio), its specific vibrations are overlapped by the stronger vibrations of the inorganic silica network.
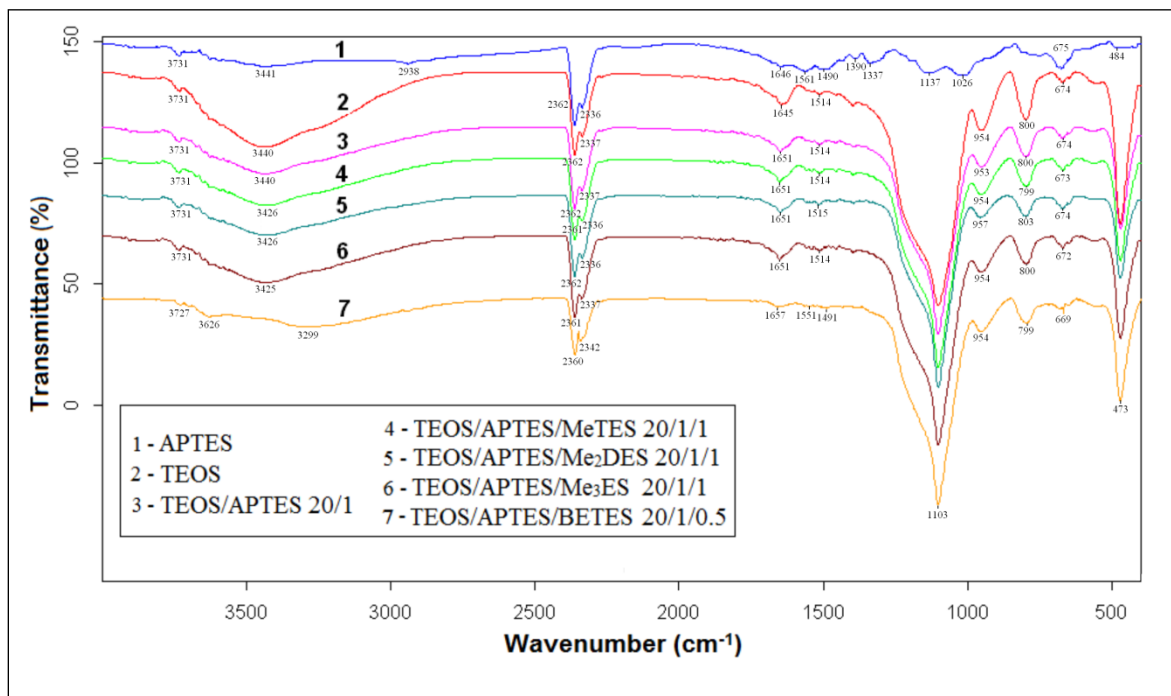
Figure 2.8. *FTIR spectra of aminopropyl functionalized silica particles*

The broad band covering the range from 3000 to 3800 cm^{-1} can be assigned to hydrogen bonded and partially hydrated silanols (Si-OH). This band was caused by overtones or combinations of vibrations of Si-OH or H_2O and is generally composed of stretching modes.

For samples grafted with aminopropyl, the silanol groups that are shown in the spectrum of **sample 2** (the broad band at ~ 3440 cm^{-1}) were partially consumed by reaction with APTES.

The region of 3000-2800 cm^{-1} corresponds to symmetrical and asymmetrical stretching vibrations of CH_2 from aminopropyl segment. In 1680-1620 cm^{-1} region, band at ~ 1630 cm^{-1} characteristic to NH_2 deformation in primary amines (due to the formation of NH_3^+ as the carbon dioxide is adsorbed onto the silica hybrid), is overlapped by the band at ~ 1650 cm^{-1}, assigned to C=O stretching in carbonyl compounds. Peak 1491 cm^{-1} was attributed to N-H vibration

(bending mode) in the primary amine group (R-NH$_2$). The band at 1390 cm^{-1} have been assigned to the bicarbonate species (C=O bending).

The main bands in the region 1300-400 cm^{-1} are associated with the combination of vibrations of the silica network: the strong band that emerged at ~ 1103 cm^{-1} (SiO$_4$ ring asymmetric stretching), ~ 954 cm^{-1} (Si-O-Si symmetric stretching within the SiO$_4$ tetrahedron), ~ 800 cm^{-1} (O-Si-O symmetrical stretching), and ~ 473 cm^{-1} (Si-O-Si bending in SiO$_4$ tetrahedron). As it was expected, the intensities of these absorption bands decrease with reducing the weight percentage of TEOS in the final hybrid.

II.3.7 Solid State Nuclear Magnetic Resonance (ssNMR)

The ^{29}Si CP/MAS NMR spectra of pristine SiO$_2$ particles (**samples 1** and **2**) and hybrid silica particles (**samples 3-6**) are shown in **Figure 2.10a**. The assignments of the signals to the D, T and Q sites are also shown. The spectrum of **sample 2** contains three signals at chemical shifts of -92.3, -100.9, and -110.6 ppm, which have been, respectively, assigned to (i) silicon atoms with two attached hydroxyl groups, designated as Q^2; (ii) silicon atoms with one attached hydroxyl groups, designated as Q^3; and (iii) silicon atoms with no hydroxyls, designated as Q^4.

The attachment of di- and trifunctional co-precursors leads to the appearance of extra signals. Thus, signal at -20 ppm is assigned to -O$_2$SiR$_2$ structures, designated as D^2, the signal around -60 ppm is assigned to -O$_2$Si(OH)R structures, designated as T^2, and signal around -68 ppm is assigned to -O$_3$SiR structures, designated as T^3.

The signal at about -20 ppm, shown in the **sample 5** spectrum, is due to the covalently attached Me$_2$DES molecules (a D^2 group), while the T^2 and T^3 signals indicate the attachment of the hydrolyzed APTES (and MeTES for **sample 4**) to the preformed TEOS based silica network. Addition of monofunctional ligands (e.g., Me$_3$ES) could not be confirmed (see the spectrum of **sample 6**, which is identical to **sample 3**).

Figure 2.10b shows the ^{13}C CP/MAS NMR spectra obtained for APTES (**sample 1**) and TEOS/APTES hybrids (**samples 3-6, 8, 9**). In the ^{13}C ssNMR spectrum of **sample 1** three signals are seen at 43 ppm (shoulder at 45.6), 22.5 ppm (shoulder at 25.2) and 11 ppm in accordance with the expectations. Note, however, that the two high-frequency signals consist of two overlapping peaks. This suggests that carbons (ii) and (iii) (see **Figure 2.10b**) exist in two

different chemical environments. The 165.1 ppm signal can be assigned to a carbamate carbon atom.
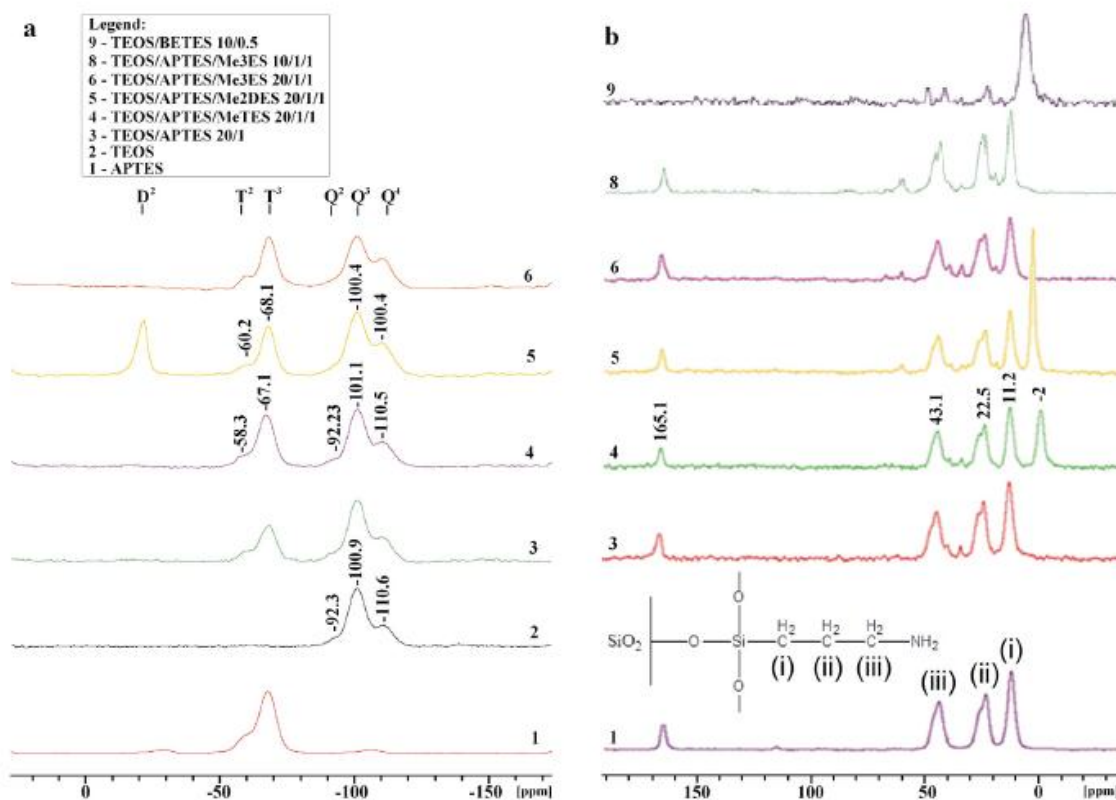
Figure 2.10 *a) ^{29}Si CP/MAS NMR; and (b) ^{13}C CP/MAS NMR solid state spectra of pristine and modified silica particles*

For **samples 4** (TEOS/APTES/MeTES) and **5** (TEOS/APTES/Me$_2$DES), the appearance of a new signal at -2.3 and 1.7 ppm, assigned to the methyl groups, indicates the integration of the hydrolyzed mono- and di-alkyl silica derivatives in the TEOS based silica network, respectively. However, regardless of the ratio used, the more bulky monofunctional silanes (Me$_3$ES, **samples 6** and **8**) did not bind to the silica surface (**Figure 2.10b**).

In a control sample, prepared only from TEOS and BETES (**sample 9**), the presence of Si-CH$_2$- groups was detected (see the strong signal at 1.7 ppm), while the 165.1 ppm carbonyl signal was no longer observed. This can be taken as further confirmation that only the amino-functionalized hybrids (all APTES containing samples) have the ability to capture the atmospheric CO_2, unlike the ligands without the terminal amine group, such as the TEOS/BETES hybrid (**sample 9**).

Chapter III. Preparation of silica particles functionalized with glycidyloxy groups

III.1 Synthesis of silica supports with glycidyloxy functions

The two step procedure described in the previous section was used for synthesis of epoxy-functionalized silica particles. In the first step, SiO_2 particles were formed (according to the Stöber method) [23,24], and after glycidyloxy functions have been generated on the preformed silica surfaces. The used molar ratio between GPTMS and TEOS was 1:20 according to Brambilla et al. [25].

In some cases, alkyl silanes were added together with GPTMS to the reaction system and the used molar ratio of various systems are presented in **Table 3.1**.

In the case of **sample 13**, the silica particles have been synthetized only from GPTMS and used as a reference sample, since we assume that the epoxy functions of the silica surface is too dense; hence prevent sterically the effective interaction of the humic acids with silanes. **Sample 18** is the only sample which has not contained GPTMS. Here was focused on demonstrating the efficient binding of the alkylsilane to the silica surface.

III.2 Characterization techniques

The structural and morphological characteristics of obtained hybrid materials were investigated using different methods:

- elemental composition – *Elemental Analysis (**C,H,N**)*;
- thermal behavior – *Thermogravimetric Analysis (**TGA**)*;
- average hydrodynamic diameter and particle size distribution – *Dynamic Light Scattering (**DLS**) Technique*;
- zeta potential – *Laser Doppler Velocimetry (**LDV**) Technique*;
- structure – *Fourier Transformed Infrared Spectroscopy (**FTIR**) and Solid State Nuclear Magnetic Resonance (**ssNMR**)*.

III.3 Results and discussions

III.3.1 Elemental Analysis (C,H,N)

The carbon contents of the synthetized silica particles are shown in **Table 3.1**. These data vary depending on nature of co-precursors and their molar ratio used in the preparation procedure.

The highest carbon content was recorded for **sample 13** derived from GPTMS, while the lowest for probe containing only TEOS (**sample 2**). The TEOS/GPTMS system (**sample 14**) showed a relatively higher carbon content.

Table 3.1 *Contents of carbon, nitrogen and hydrogen for the various silica systems*

Sample no.	Silica system	Molar ratio	Carbon (%)	Nitrogen (%)	Hydrogen (%)
13	GPTMS	-	37.66	4.94	6.58
2	TEOS	-	0.94	0.55	1.36
14	TEOS/GPTMS	20/1	11.32	1.74	2.62
15	TEOS/GPTMS/MeTMS	20/1/1	7.66	1.63	2.08
16	TEOS/GPTMS/Me$_3$MS	20/1/1	6.02	1.04	1.88
17	TEOS/GPTMS/BETMS	20/1/0.5	6.69	1.11	1.96
18	TEOS/BETMS	2/1	11.07	0	2.39

When alkylsilanes were also introduced to the reaction mixture (**samples 15-17**), the measured carbon percentage was slightly lower than that for **sample 14**, because the density of glycidyloxypropyl was decreased due to the appearance of alkyl groups. Among the samples containing both GPTMS and alkyl derivative (**samples 15-17**), the highest data was estimated for METMS modified hybrid system (**sample 15**).

III.3.2 Thermogravimetric Analysis (TGA)

The weight losses and inorganic residues in the respective temperature are shown **Table 3.2**.

A positive correlation was found between weight loss and carbon content thereby higher carbon content was associated with a greater weight loss. Meanwhile, the weight loss was correlated inversely with inorganic residue measured at 700 °C.

In this study the weight loss was also studied in three temperature ranges: 25-250 °C, 250-450 °C and 450-700 °C (**Figure 3.3**).
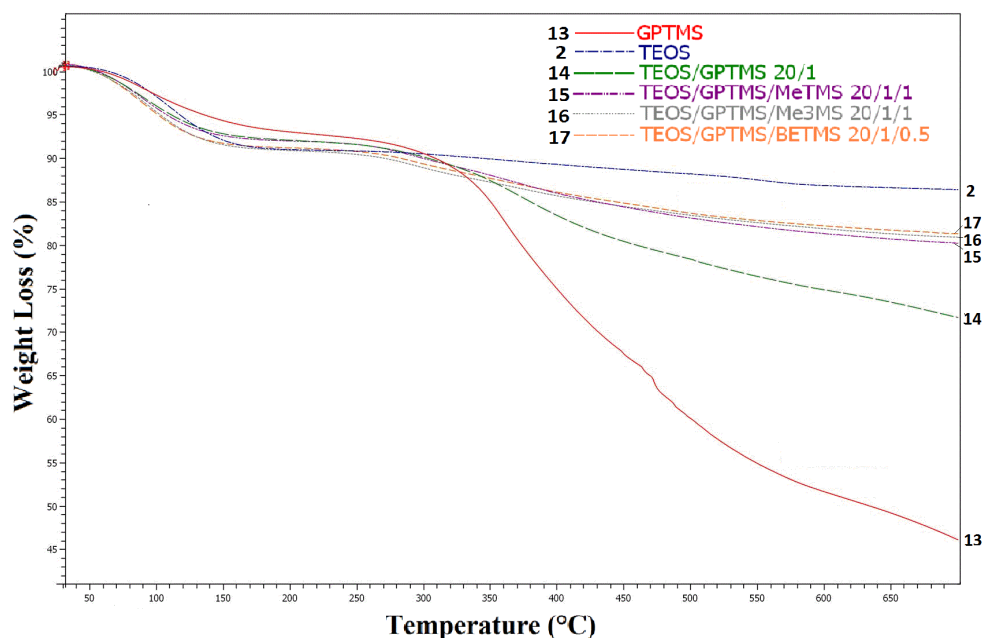
Figure 3.3 *TGA curves of glycidyloxy-silica hybrid materials*

In the first phase, the intra and intermolecular moisture was evaporated with increase of temperature. In the second stage, the organic component of the hybrid materials has degraded. The last section was due to dehydroxylation of Si-OH residual functions, accompanying the formation of Si-O-Si groups. Samples with greater weight loss indicate lower inorganic residue measured at 700 °C.

Table 3.2 *Values of weight loss and related inorganic residue measured at 700 °C*

Sample no.	Silica system	Molar ratio	Weight Loss (%)			Inorganic residue at 700°C (%)
			25-250 °C	250-450 °C	450-700 °C	
13	GPTMS	-	32.4	10.9	5.4	51.3
2	TEOS	-	9.6	2.3	2.3	85.8
14	TEOS/GPTMS	20/1	8.6	14.1	6.2	71.1
15	TEOS/GPTMS/MeTMS	20/1/1	8.9	5.4	6.2	79.5
16	TEOS/GPTMS/Me$_3$MS	20/1/1	9.8	4.8	6.1	79.3
17	TEOS/GPTMS/BETMS	20/1/0.5	9.7	5.7	4.1	80.5
18	TEOS/BETMS	2/1	17.6	5.0	6.6	70.8

III.3.3 Particle size measurements (Dynamic Light Scattering (DLS) Technique)

In **Table 3.3** are shown the average diameter values registered for 1/25 diluted samples in water.

Table 3.3 *Particle size and zeta potential values for the various silica systems*

Sample no.	Silica system	Molar ratio	Average Diameter (nm)	Zeta Potential (mV)
13	GPTMS	-	0.3	-
2	TEOS	-	549	-45
14	TEOS/GPTMS	20/1	620	45
15	TEOS/GPTMS/MeTMS	20/1/1	649	45
16	TEOS/GPTMS/Me$_3$MS	20/1/1	595	54
17	TEOS/GPTMS/BETMS	20/1/0.5	659	34
18	TEOS/BETMS	2/1	460	-37
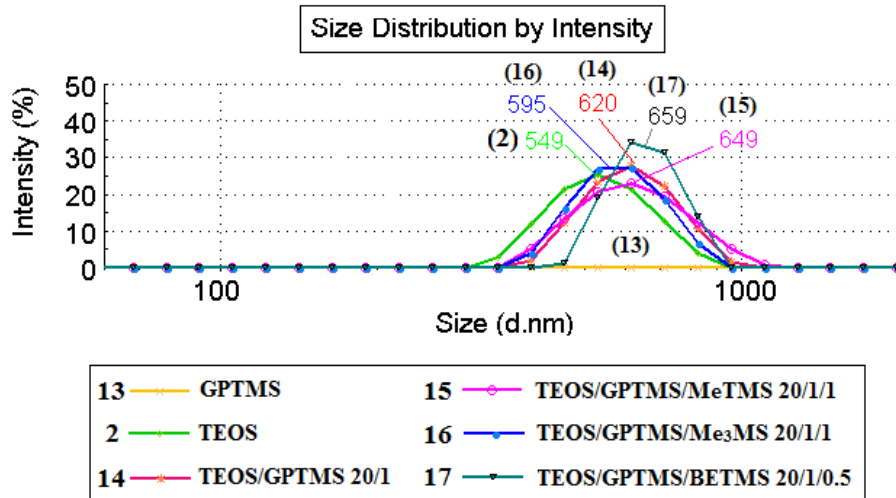
Figure 3.4 *Size distributions by intensity for glycidyloxypropyl-silica particles*

The particle size of **sample 2** was 549 nm. For **sample 14**, the size increased to 620 nm, proving the efficient attachment of GPTMS to the surface. After addition of MeTMS along with GPTMS (**sample 15**), the average diameter further increased until 649 nm. When Me$_3$MS was used as a spacer (**sample 16**), the resulted particle had similar average size as for the **sample 15**, indicating that this co-precursor did not covalently link to the silica network. It acted as a

25

stabilizer for the silica particles, being only adsorbed on their surface. The highest average diameter was measured for **sample 17** (659 nm). BETMS is a well-known cross-linker, which leads to the formation of very compact silica network; this fact has been proved by narrowing the particle size distribution (**Figure 3.4**).

III.3.4 Zeta potential measurements (Laser Doppler Velocimetry (LDV) Technique)

The zeta potential for these silica particles were recorded for samples diluted in water (dilution 1/25) and ranged between -45 and +54 mV (**Table 3.3**).

When the glycidyloxypropyl functions were grafted on the silica particle surfaces, it was accompanied with the change of zeta potential from negative to positive values (**samples 14-17**). In comparison to **sample 14**, the zeta potential value of **sample 15** has not changed.

For the **sample 16**, the zeta potential shifted to more positive value (54 mV), proving that this co-precursor was predominantly adsorbed on the silica particle surface, and has not covalently bonded to the surface.
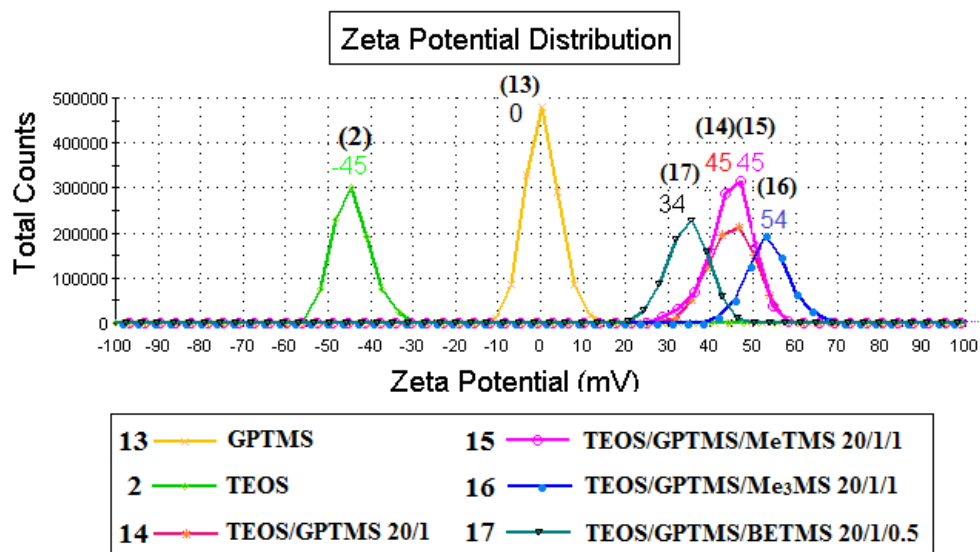

Figure 3.5 *Zeta potential distributions for glycidyloxypropyl-silica particles*

By inserting BETMS (**sample 17**), the co-precursor with spacing and crosslinking role, the zeta potential value decreased, due to a lower density of glycidyloxypropyl groups on the silica surface (**Figure 3.5**).

III.3.5 Fourier Transformed Infrared Spectroscopy (FTIR)

In **Figure 3.6** is shown a comparison between spectra of pure silicas (containing only one precursor: GPTMS (**sample 13**) or TEOS (**sample 2**)) and the various silica hybrids derived from TEOS and GPTMS (**samples 14-17**).
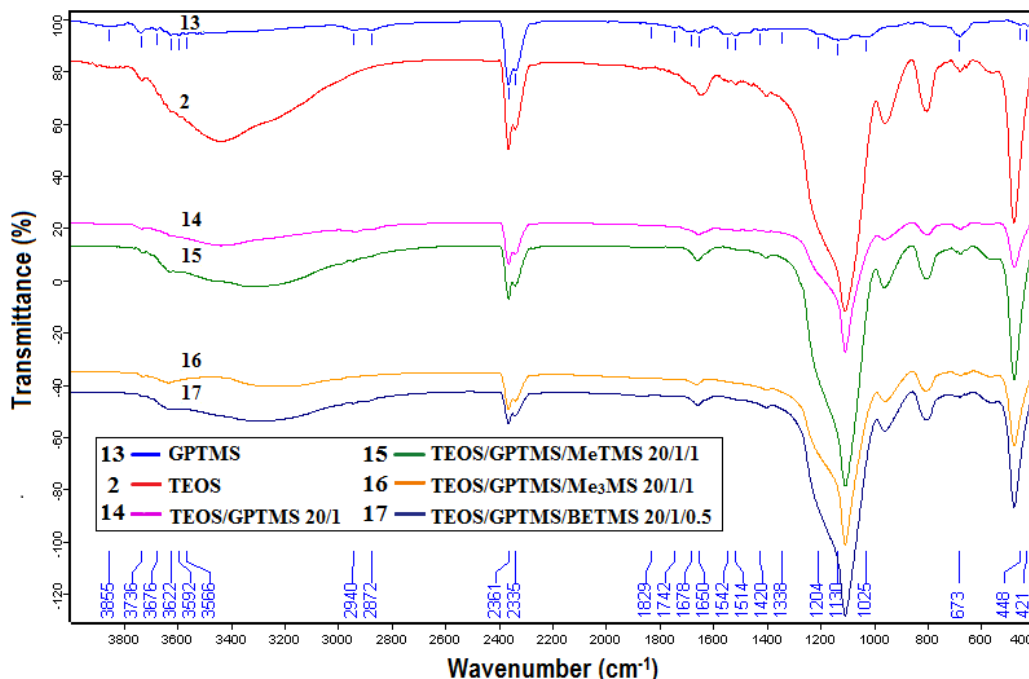
Figure 3.6 *Comparison of FTIR spectra of glycidyloxypropyl-silica particles*

FTIR spectra are used to highlight the formation of the organic-inorganic matrix (**Figure 3.6**) and also show the characteristic signals generated by symmetrical and asymmetrical stretching of Si-O-Si groups. Obviously, the most intensified Si-O-Si adsorption band (1200-1000 cm^{-1}) was measured for **sample 2** with the greatest content of TEOS.

The FTIR spectra of samples (**samples 15 and 17**) show a broad band in the region 3500-2500 cm^{-1}, centered at 3302 cm^{-1} generated by C-H stretching vibration in methyl or ethyl segments. For sample (**sample 16**) this band is shifted toward lower wavenumber (3216 cm^{-1}).

III.3.6 Solid State Nuclear Magnetic Resonance (ssNMR)

The **Figure 3.7** presents a comparison between ^{29}Si CP/MAS NMR spectra of pure TEOS (**sample 2**) and silica hybrids prepared in the presence of GPTMS and MeTMS (**sample 15**).

The ^{29}Si spectrum of pure silica particle (**sample 2**) contains three signals at chemical shifts of -92.3 assigned to Q^2, -100.9 assigned to Q^3, and -110.6 ppm assigned to Q^4, respectively.

In the **sample 15**, signals at -55 ppm (T^2) and at -65 ppm (T^3) confirmed the covalent attachments of organic groups onto the silica surface. Peaks around at -92 ppm (Q^2), -100 ppm (Q^3), -110 ppm (Q^4) confirmed the formation of silica framework.
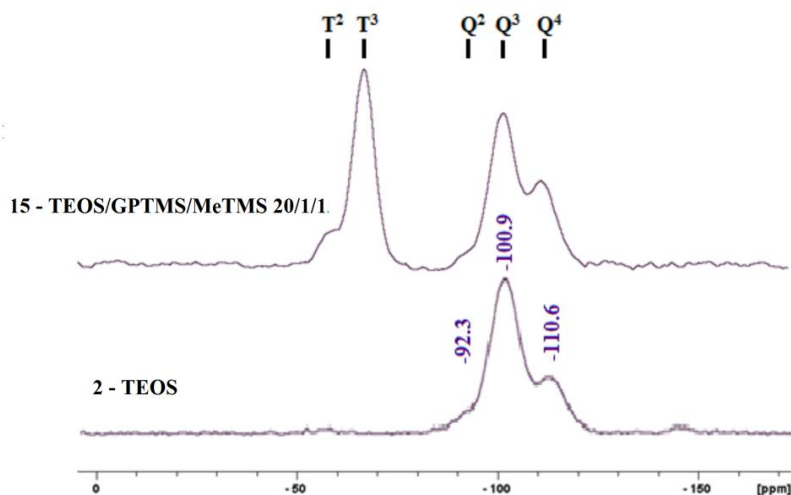
Figure 3.7 ^{29}Si CP/MAS NMR solid state spectra of pure and grafted silica particles

In **Figure 3.8** is shown a comparison between ^{13}C CP/MAS NMR spectra of pure GPTMS (**sample 13**) and silica hybrids prepared from GPTMS and MeTMS (**sample 15**). The methyl (-5 ppm) and glycidyloxypropyl functions have been identified from the spectra. So, it demonstrates the successful generation of epoxy– and methyl groups on the silica surface.
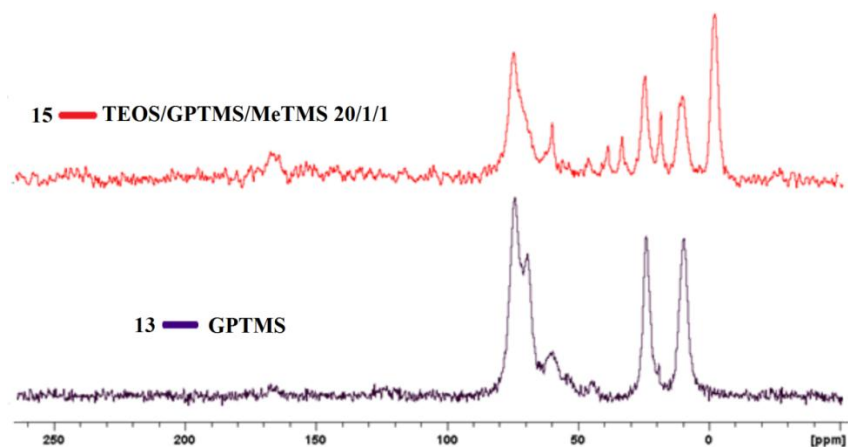

Figure 3.8 ^{13}C CP/MAS NMR solid state spectra of pure and grafted silica particles

Chapter IV. Silica hybrid particles functionalized with humic acids

IV.1 Coupling method

100 mL of stock solutions of humic acids (AHA – humic acids from Aldrich and PHA – humic acids extracted from a local peat deposit) in buffer (pH 7.5) were prepared at a concentration of 1 g/L. The resulted stock solutions were further used for the acid immobilizing tests. The absorbency was recorded by UV-VIS technique at a fixed wavelength (254 nm) [26].

The difference between the initial concentration of the stock solution and the measured concentration of the filtered solution gives the concentration of HA chemically attached onto the silica supports.

IV.2 Results and discussions

IV.2.1 The humic acid immobilization tests of the silica supports with amino functions

Two sorts of humic acids (AHA and PHA) were selected for testing the functionalization efficiency of the synthesized aminosilica hybrids. The relative concentrations of immobilized HA on various silica supports are represented in **Figure 4.6**.
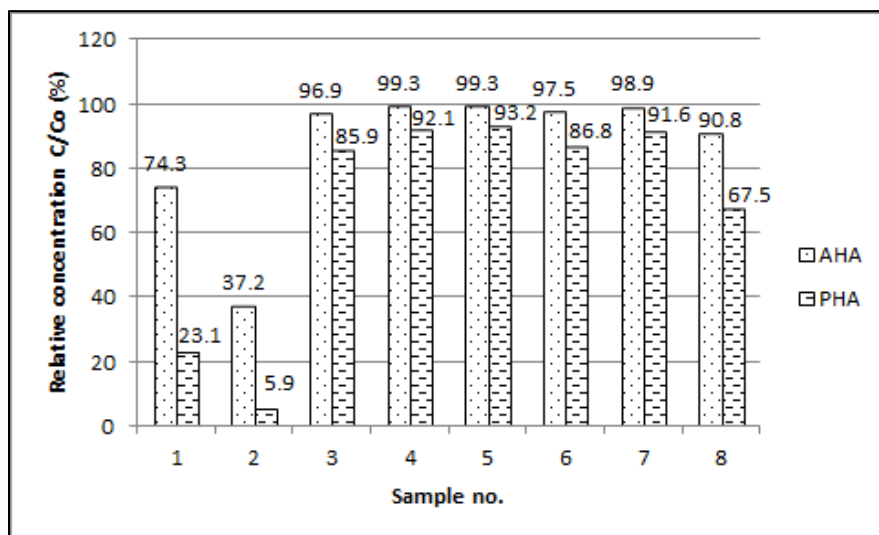

Figure 4.6 *Relative concentrations of immobilized humic acids (AHA and PHA, respectively) as a function of silica support type*

Obviously, the lowest concentration of up-taken HA was determined for **sample 2**, having only Si-OH groups on the surface. **Sample 1**, synthesized only from APTES, shows an

almost twice higher concentration of chemically immobilized HA if compared with **sample 2**, due to its amino functions. In previous studies [18] it was shown that the large molecules of humic acids are sterically hindered to attach to the amino functions present in the aminosilica supports. More than that, through zeta potential measurements, we showed above (see Section II.3.4.), that a significant amount of the amino functions are hidden inside the silica frame resulted from self-condensation of APTES, while towards the exterior remains mostly Si-O ions, less reactive with HA molecules. Therefore, it is not surprising that for the hybrid (**sample 3**) (TEOS/APTES 20/1), which has a much lower density of the aminopropyl groups on the surface than **sample 1** and has a positive value of zeta potential (most of the amino functions are located toward the exterior of the silica particles), the HA-binding ability is greatly improved.

Figure 4.7 *Pictures of the two humic acid stock solutions (a) and immobilization tests of AHA (b) and PHA (c), respectively on various silica supports*

Despite our expectations, for samples where methyl-, dimethyl- or ethyl groups were used as spacers for the amino-functions (**samples 4, 5 and 7**), the improvements of the immobilization capacity are not impressive enough (~ 2% for AHA and ~ 6% for PHA immobilization) to justify the usefulness of aminopropyl spacing by alkyl groups. So, the density of aminopropyl functions seems to be small enough at this low APTES molar ratio (TEOS/APTES = 20/1) and does not cause steric hindrance in the case of the HA molecules. Therefore spacing the amino functions with alkyl groups is not an absolutely necessary (**Figure**

4.7). In addition, the inefficient grafting of Me₃ES co-precursor on the silica hybrid network is also confirmed by the coupling tests, in which similar (**sample 6**) or lower concentration (**sample 8**) of immobilized HA was determined compared with the reference support obtained from TEOS and APTES (**sample 3**).

IV.2.2 The humic acid immobilization tests of the silica supports with glycidyloxy functions

The relative concentrations of humic acids attached chemically onto surface of various silica supports are shown in **Figure 4.9**. The lowest HA concentration in both cases was measured for **sample 2** containing only silanol groups on its surface. **Sample 13** was synthesized exclusively from GPTMS having epoxy functions on the side chains and shows a slightly higher adsorbed HA concentration compared to **sample 2**.
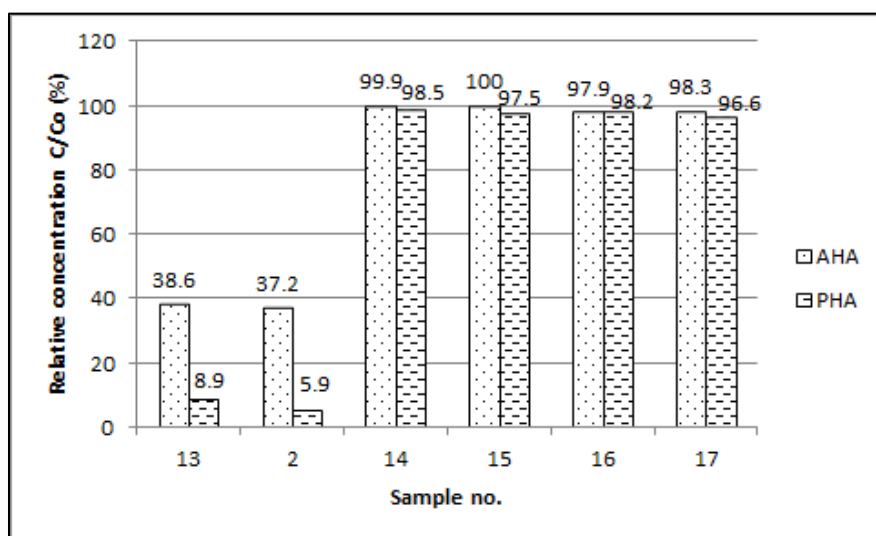
Figure 4.9 *Relative concentrations of adsorbed AHA and PHA on various silica surfaces*

In our previous study [27], it was found that spacing the amino function by alkyl groups have not greatly improved the coupling efficiency of the silica supports, because the low density of aminopropyl functions present in the silica surfaces have not caused steric hindrance. Hence there is no need to separate the coupling agents with spacers.

In our present case, similar results were obtained for glycidyloxypropyl functionalized silica particles. During the preparation process, when were used both co-precursors (TEOS and GPTMS), the coupling efficiency significantly increased (**sample 14-17**). But when beside TEOS and GPTMS, an alkylsilane (**sample 15-17**) were also added to the reaction solution, the HA adsorption capacity tests gave similar results as for **sample 14** (**Figure 4.10**). For these

reasons, there are no significant differences in HA coupling efficiency between sample derived from TEOS and GPTMS (**sample 14**) and samples where the epoxy functions were spaced by alkyl groups (**samples 15-17**).
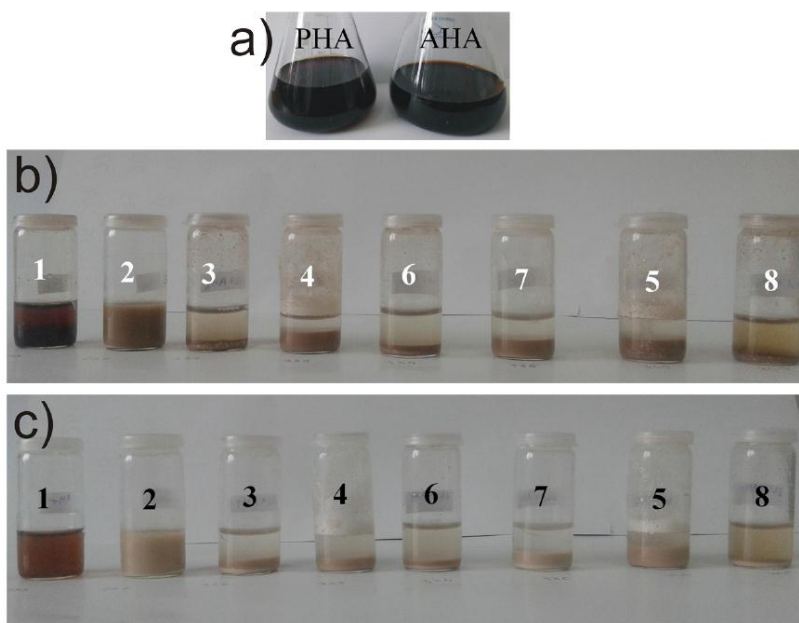

Figure 4.10 *Pictures of two humic acid stock solutions (a) and the coupling tests of AHA (b) and PHA (c), respectively on different silica supports*

Chapter V. Preparation of polyether polyol based silica hybrids

V.1 Synthesis

V.1.1 Preparation of functionalized polyether polyols

Functionalized polyether polyols were obtained in a similar way to that was previously reported in literature [21,28,29]. Th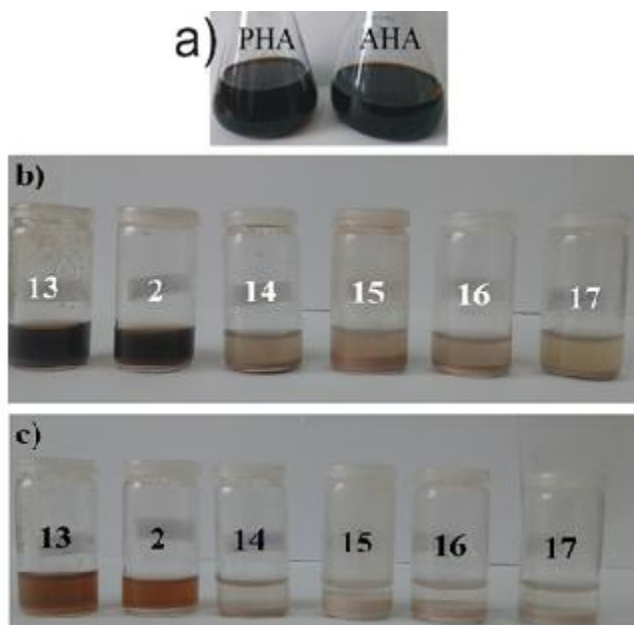e purpose of polyether polyols functionalization with (3-isocyanatopropyl)triethoxysilane (NCOTEOS) was to connect the triethoxy silane groups from NCOTEOS to the polyetheric chains.

Preparation of these functionalized products was carried out in a glass reaction recipient with necks and refrigerator. Polyether and DABCO were mixed together and heated up to 50 °C. Then, NCOTEOS was added dropwise in the reactor. The reaction was maturated for 6 h at 50–55 °C, under N_2 atmosphere and continuous stirring. Functionalization efficiency was evaluated by FTIR, the disappearance of NCO signal at 2270 cm^{-1} peak being observed after 5–6 h.

Urethane bonds (1531 cm^{-1}, 3355 cm^{-1}) are formed by reaction between the hydroxyl (-OH) functions from polyols and isocyanate (–N=C=O) functions from the NCOTEOS. End-capping of the polyols with ethoxy groups will contribute to the formation of covalent bonds between the block copolymers and the silica frame generated through the sol-gel reactions of MeTES and VTES.

V.1.2 Synthesis of the hybrid materials

Polyether polyol – silica hybrids were prepared by the sol-gel method which was previously published in the literature [21]. Thus, in all preparations, MeTES and VTES were pre-hydrolyzed for 1 h in an acid water solution, in the presence of ethanol, under continuous stirring, at room temperature. Beside these sol-gel precursors, was added the polyether as such or functionalized with NCOTEOS. It was demonstrated before that the vinyl-terminated alkoxide (VTES) has a very high reactivity and its organic group can be more easily integrated in a growing inorganic network [28,29]. The molar ratio between the precursors (MeTES/VTES) was 1:1 (**Table 5.1**). In the second step, TIP and FIN were added to the solution along with the second portion of water, and the mixture was stirred for an additional hour.

The final mixtures (**Table 5.2**) were placed into open plastic vials and dried overnight, at room temperature (25°C). After drying, the plastic vials were passed under a UV lamp (λ = 365

nm, irradiation time = 15 min) in order to accomplish the UV-initiated radical polymerization of the double bonds from VTES. One part of the resulted materials was crashed into a mortar and then the powder was irradiated with 0.5 kGy/h dose in order to observe the oxidative degradation by chemiluminescence method.

Table 5.1 *Compositions for preparing the polyether polyol - silica hybrid materials*

MeTES (mole/L)	VTES (mole/L)	EtOH (mole/L)	H_2O (mole/L)	TIP (mole/L)	FIN (mole/L)	Polyether (as such or functionalized) (mole/L)
1.292	1.316	5	5.55	0.158	0.092	0,024

Table 5.2 *Silica hybrid systems based on polyether polyols*

Sample no.	Hybrid type	Polyol
19	M+PEO	un-functionalized
20		functionalized with NCOTEOS
21	M+PPO	un-functionalized
22		functionalized with NCOTEOS

Note: The base formulation - comprising the sol-gel precursors (MeTES and VTES), water, ethanol, cross-linking agent (TIP) and the photo-initiator (FIN)) - was noted with **"M"**, for all the hybrid samples, in order to simplify the figures legends.

V.2 Characterization techniques

- coupling degree of polyols – *gravimetric method*;
- structure – *NMR measurements*;
- rheological behavior – *rheological measurements*;
- oxidative degradation – *chemiluminescence method*.

V.3 Results and discussions

V.3.1 The degree of covalent coupling of the modified polyols to the silica network

As expected, for samples functionalized with NCOTEOS (**samples 20** and **22**), the values of the degree of covalent coupling are much higher than for the references (samples with un-modified polyols – **samples 19** and **21**). This is due to the presence of the ethoxysilane groups, introduced at the end of the polyol chains, which allowed a better coupling of the polyol molecules to the silica frame (**Figure 5.2**). Also, the hybrids belonging to the PPO series, exhibits much lower values of the degree of covalent coupling than those obtained for the PEO series. The much higher reactivity of the primary hydroxyls of PEO towards isocyanate functions

(–N=C=O) allowed a much better connection through urethane bonds of NCOTEOS to the polyol molecule and, as a consequence, a more efficient coupling of the functionalized block copolymer to the hybrid network (~ 89 %).
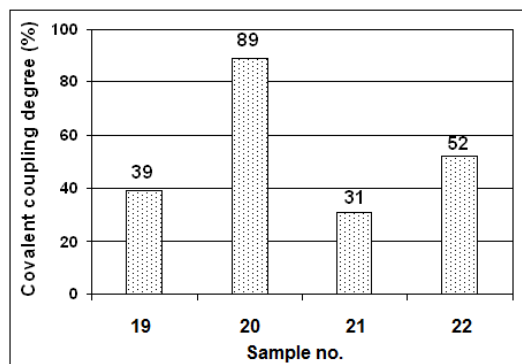

Figure 5.2 *The degree of covalent coupling of the polyols to the silica frame for samples 19-22*

V.3.2 ^{13}C NMR spectra of the polyol based silica hybrids

The spectra show that the PEO polyol, which has terminal primary hydroxyl groups and, as a consequence, a high reactivity, is almost completely functionalized with NCOTEOS (**sample 20**). After functionalization with NCOTEOS, in the NMR spectrum of the PEO polyol appears the signal corresponding to -CH$_3$ (from ethoxy group connected to Si) at 58.3 ppm (**Figure 5.3**).

For the polyol PPO, which contain both -OH primary and secondary groups, can be noticed the presence of -CH group from terminal units. It is also possible to assign -CH$_2$ group of terminal units (~ 68.4 ppm). Depending on the primary and secondary groups, the methyl groups were assigned to the terminal units as follows: 18 ppm for –OH primary group and 18.6 ppm for –OH secondary group (**sample 21**).

The integral of corresponding signal is in good agreement with the proposed structure. It can be concluded that the -OH groups are present in a molar ratio of 8% comparing with the total number of propylene oxide units contained in the polyether, the CH-OH/CH$_2$ molar ratio being 1.

By functionalization of PPO with NCOTEOS (**sample 22**), CH-OH/CH$_2$ ratio decrease to ~ 0.76 and it is observed the signal corresponding to CH$_2$ unit from triethoxy silane (whose integral is proportional to the difference caused by the absence of CH-OH). Calculating the variation of concentration of these groups, a coupling degree of only ~ 13% was observed. The

structure is confirmed by the presence in the methyl region of signal at 18.16 ppm, corresponding to the -CH$_3$ group from the ethoxy silane.

Figure 5.3 *^{13}C NMR spectra of the resulted polyol-silica hybrids*

V.3.3 Rheological measurements

Evaluation of the rheological behavior was performed during the synthesis of the hybrid systems specified in **Table 5.2**. The sol-gel systems were prepared at two different temperatures: 23 °C and 60 °C and subjected to two different shear rates: 20 rpm and 50 rpm (**Figure 5.4**). Observing the time assigned to the beginning of gelation (sol-gel reaction) for the various systems studied, a much shorter reaction time was revealed for the PEO series.

When the sol-gel process was performed at a higher temperature (T = 60 °C), the viscosity evolution experienced a period of inertia, then a sharply increase. Especially for the most reactive polymeric component (PEO functionalized with NCOTEOS, **sample 20**), the cross-linking reaction occurs within a few minutes after the addition of the sol-gel cross-linking agent (TIP).

When the sol-gel reactions were carried out at the room temperature (T = 23°C), the increase of viscosity was generally slow. But even at this low temperature, the gelation time of the sol-gel system derived from PEO functionalized with NCOTEOS (**sample 20**), is much shorter than that of the system based on PPO functionalized with NCOTEOS (**sample 22**).
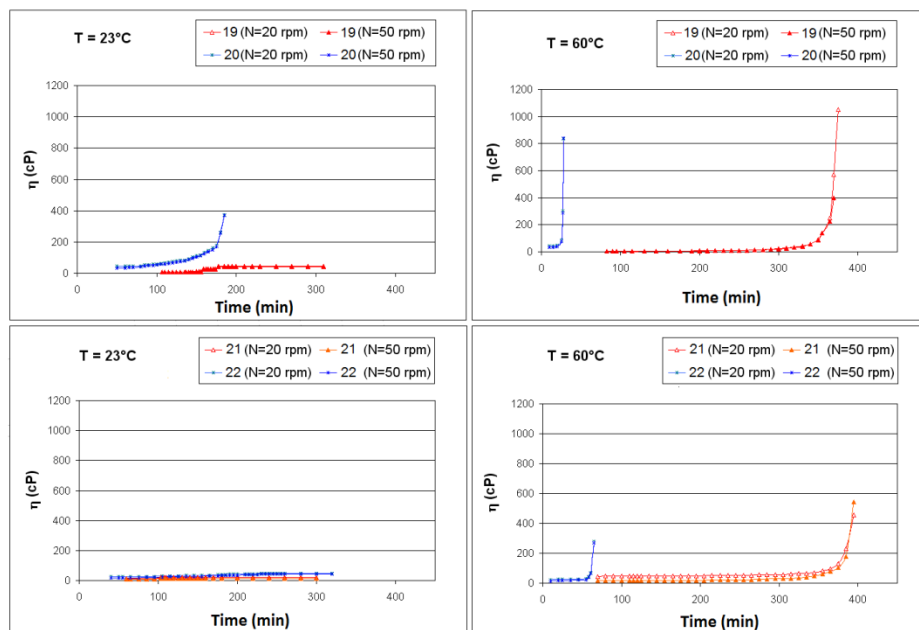
Figure 5.4 *Evolution in time of the viscosity of the synthesized hybrid systems*

V.3.4 Evaluation of oxidative degradation

The onset oxidation temperatures (OOT) of the hybrid systems based on polyether polyols, recorded by the chemiluminescence method are presented in **Figure 5.5a**. The values obtained for onset oxidation temperature (OOT), are good indicators for the level of compound stability. It means that these temperatures represent the threshold, where oxidation effectively starts, depicting the peculiar resistance to thermal degradation [30].

Analyzing **Figure 5.5b**, it can be observed that OOT decreases with the increasing of the irradiation dose. For sample based on the un-modified PEO, the onset oxidation temperature was observed at ~ 130°C and decreases gradually, when sample was irradiated with different doses, reaching ~ 81°C. In case of sample with PEO functionalized with NCOTEOS, the OOT was recorded at ~ 126°C and decreases slower compared with the unmodified polyol.

Samples from PPO series present less reactive groups compared with the samples containing PEO. Thus, for sample with PEO, the OOT begin at ~ 130°C, while for sample with PPO, the OOT begin at ~ 116°C. It is obvious that the samples with PEO are more stable to degradation than the samples with PPO.
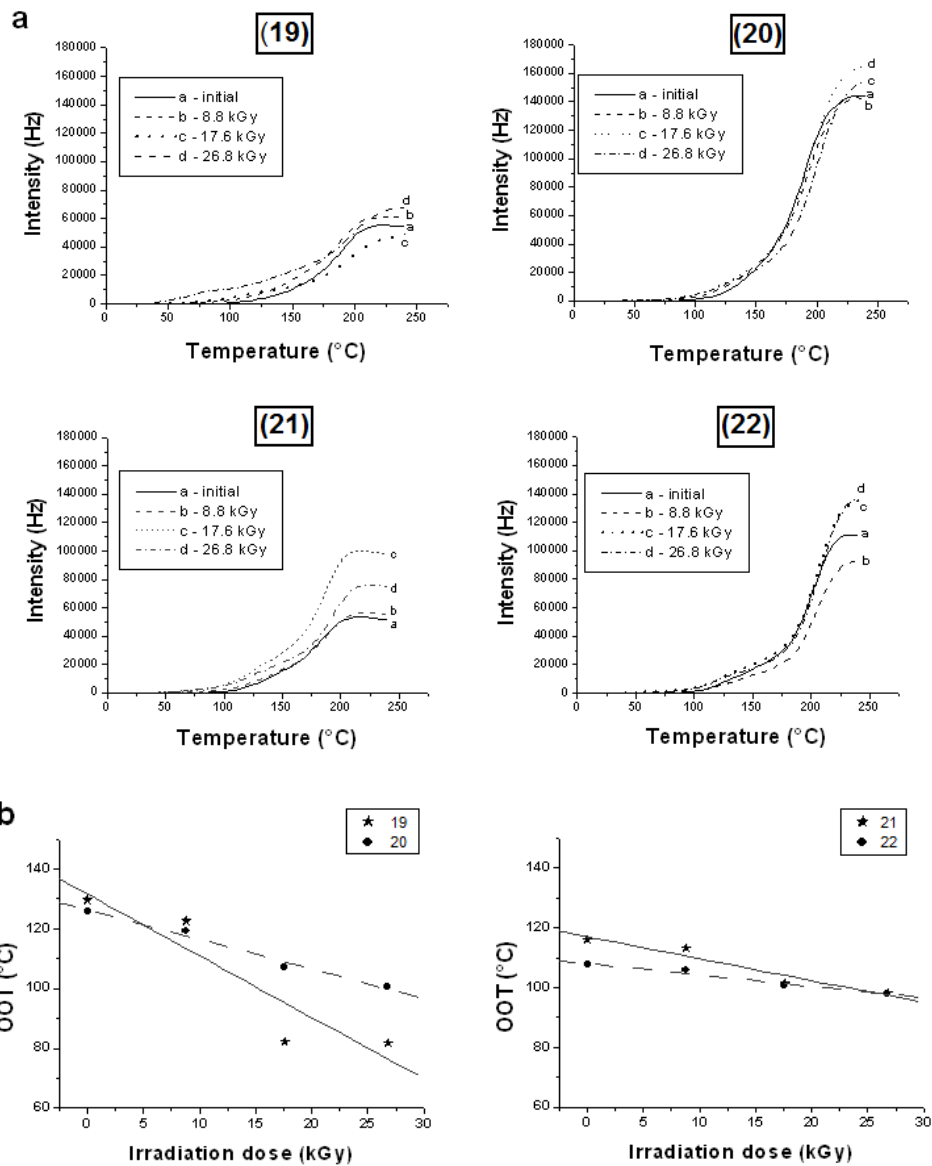
Figure 5.5 *Increase of chemiluminescence intensity versus temperature (a) and decrease of OOT as function of irradiation dose (b)*

The addition of the coupling agent (NCOTEOS) seems to cause a lower degradation of the functionalized sample after irradiation. These results also confirm that the functionalization reaction occurred successfully.

General conclusions

This PhD thesis is focused on preparation and characterization of a series of novel silica nanoparticles, prepared through a basic or acidic two step sol-gel process in water. The reactive organosilane compounds have been used for modifying and tailoring the surface properties of inorganic materials, thereby the material will contain the desired functional groups on its surface. The reactive functions (also called coupling agents) ensure the attachment of organic substances to the silica hybrid surfaces.

In the first part, silica hybrid materials grafted with functional groups were prepared which are capable of interacting with humic acids. In this regard, we have completed two research directions:

- ➢ synthesis of silica particles functionalized with reactive amino groups;
- ➢ synthesis of silica particles functionalized with reactive glycidyloxy groups.

Amino-silica hybrids were developed by grafting of the amino functions (alone or spaced by alkyl functions) onto preformed mono-dispersed SiO_2 particles. It was evaluated the effect of the type and molar ratio of co-precursors used during the sol-gel process on the silica network structure and dimension and morphology of these resulting particles.

The presence of the aminopropyl chains and methyl, dimethyl and ethylene moieties on the silica surface was evidenced using different characterization methods.

Further, it has also been studied the synthesis of silica particles functionalized with (3-glycidyloxypropyl)trimethoxysilane (GPTMS), alone or together with alkylsilane, containing one or more methoxy groups. The physicochemical characterization of the resulted hybrid systems was carried out, and the correlation of structure and properties was characterized depending on the chemical structure and distribution of co-precursors in the reaction system.

The synthesized hybrid materials were based on silica network into which the glycidyloxy and methyl moieties were successfully incorporated.

In both cases, it was also evidenced that, perhaps for steric reasons and for its lower reactivity (containing only one Si-OEt reactive group), the monofunctional derivatives (Me_3ES or Me_3MS) did not connect to the silica network.

In the second part of the thesis it was studied the humic acids coupling efficiency of the different types of silica particles synthesized in the previous step. They contain reactive groups (amino or glycidyloxy), which facilitate the immobilization of the humic acids.

Our researches showed that the synthetized silica particles-supports were able to efficiently interact with external large HA molecules, regardless of the origin. However supports functionalized with amino or glycidyloxy were as effective as the silica systems with coupling agents spaced by nonhydrolysable groups, indicating that the addition of spacers did not significantly change the amount of adsorbed HA.

Due to their characteristics, these materials can apply for immobilizing of humic acids through their amino or epoxy functions with the final purpose of using them in environmental studies.

The third part of the thesis presents the preparation and properties of new silica hybrid materials, synthesized in the presence of two commercially available polyether polyols (as such or functionalized with (3-isocyanatopropyl)triethoxysilane (NCOTEOS)). The differences between the two types of polyether polyols consist of terminal hydroxyl group and of different molecular structure.

Incorporation of the functionalized polyether polyols to the hybrid matrix was more efficient than in the case of unmodified polyether polyols. PEO also has a better reactivity in the sol-gel process and therefore is more efficiently connected to the inorganic silica network. Due to the lower reactivity of their secondary -OH groups, the degree of attachment to the silica network determined for polyols belonging to PPO series is much lower compared to the corresponding polyols belonging to PEO series.

The samples containing PEO are more stable to oxidative degradation than the samples with PPO. Moreover, functionalization of the polyols with NCOTEOS occurred and can improve the quality of the final hybrid material.

 We can conclude that this PhD thesis has made significant original contributions in sol-gel technology. The controlled synthesis and systematic variation of composition and chemical structure of the precursors involved in the sol-gel process permitted the development of new materials with controlled properties. In addition, the procedure used for preparing them do not have adverse environmental impacts, due to elimination of using high cost and polluting solvents by replacing them with aqueous systems.

Selective references

1. Akimov, Y.K., Fields of Application of Aerogels (Review). *Instrum. Exper. Techniques*, 46, 287-299, **2003**.

2. Szabo, G., Angelova, A., Guczi, J., Bulman, R.A., An Examination of the Uptake of radioiodine by Chemically Bound Humic Acid and by some Solid Phase of Soil, *The Science of the Total Environment*, 130/131, 375-382, **1993**.

3. Garnier-Sillam, É., Hariyento, S., Bourezgui, Y., Humic substances in peats (Sumatra, Indonesia), *Analysis*, 27, 5, 405-408, **1999.**

4. Prado, A.G.S, Miranda, B.S., Zara, L.F., Adsorption and thermochemical data of divalent cations onto silica gel surface modified with humic acid at solid/liquid interface, *Journal of Hazardous Materials B120*, 243–247, **2005**.

5. Armon, R., Zolkov, C.H., Laor, Y. Entrapment of Humic Acid in a Sol-Gel Matrix − A New Tool for Sorption Studies, *Journal of Sol-Gel Science and Technology*, 19, 95–100, **2000**.

6. Helles, R., Wastewater COD Removal using Sol-Gel Immobilized Humic Acid, *J. of Toxicology and Environmental Health Sciences*, 2, 7-10, **2010**.

7. Rosa, G., Gardea-Torresdey, J.L., Peralta-Videa, J.R., Herrera, I., Conteras, C., Use of Silica-Immobilized Humic for Heavy Metal Removal from Aqueous Solution under Flow Conditions, *Bioresource Technology*, 90, 11-17, **2003**.

8. Klavins, M., Eglite, L., Immobilisation of Humic Substances, *Colloid and Surfaces A*, 203, 47-54, **2002**.

9. Rosa, A.H., Vicente, A.A., Rocha, J.C., Trevisan H.C., A new application of humic substances: activation of supports for invertase immobilization, *Fresenius J. Anal. Chem.,* 368, 730–733, **2000**.

10. Brinker, C.J., Hydrolysis and condensation of silicates: effects on structure, *Journal of Non-Crystalline Solids,* 100, 31-50, **1988**.

11. Prado, A.G.S., Miranda, B.S., Dias, J.A., Attachment of Two Distinct Humic Acids onto a Silica Gel Surface, *Colloid and Surfaces A*, 242, 137-143, **2004**.

12. Surivet, F., Lam, T.M., Pascault, J.P., Control synthesis of isocyanate and alkoxy-silane terminated macromers, J. *Polym. Sci. A: Polym. Chem.,* 29, 13, 1977-1986, **1991**.

13. Sarkar, B., Alexandridis, P., Self-assembled block copolymer-nanoparticle hybrids: Interplay between enthalpy and entropy, *Langmuir,* 28, 45, 15975–15986, **2012**.

14. Rekondo, A., Fernández-Berridi, M.J., Irusta, L., Synthesis of silanized polyether urethane hybrid systems. Study of the curing process through hydrogen bonding interactions, *European Polymer Journal,* 42, 2069–2080, **2006**.

15. Fazakas, J., Fazakas, E., Muntean, M., Ceramic Support as Catalyst in Heterogeneous Catalytic Systems, *Materiale de construcţii Bucureşti,* 28, 2, 88-90, **2000.**

16. Brinker, C.J., Scherer, G.W., Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, *Academic Press,* **1990**.

17. Fazakas, J., Lianţi in sistemul SiO_2-H_2O, *Teza de doctorat*, Universitatea Tehnica Timişoara, Facultatea de Chimie Industriala, **1998**.

18. Koopal, L.K., Yang, Y., Minnaard, A.J., Theunissen, P.L.M., Van Riemsdijk, W.H., Chemical Immobilization of Humic Acid on Silica, *Colloids and Surface A,* 141, 385-395, **1998**.

19. Zheng, H., Gao, C., Peng, B., Shu, M., Che S., pH-responsive drug delivery system based on coordination bonding in a mesostructured surfactant/silica hybrid, *J. Phys. Chem. C,* 115, 15, 7230-7237, **2011**.

20. Fadeev, A.Y., McCarthy, T.J., Self-Assembly is not only Reaction Possible between Alkyltrichlorosilanes and Surfaces: Mononuclear and Oligomeric Covalently Attached Layers of Dichloro- and Trichlorosilanes on Silicon, *Langmuir,* 16, 7268-7274, **2000**.

21. Nistor, C.L., Donescu, D., Petcu, C., Stefan, V., Ghiurea, M., Film forming nanohybrids obtained with polyethers, *Int. J. Polym. Mater.,* 56, 8, 825-839, **2007**.

22. Fatunbi, H.O., Bruch, M.D., Characterization of the Structural Morphology of Chemically Modified Silica Prepared by Surface Polymerization of a Mixture of Long and Short Alkyl Chains Using ^{13}C and ^{29}Si NMR Spectroscopy, *Langmuir,* 29, 4974-4987, **2013**.

23. Hench, L.L., West, J.K., The Sol-Gel Process, *Chemical Reviews*, 90, 33, **1990.**

24. Brambilla, R., Pires, G.P., dos Santos, J.H.Z., Lacherda-Miranda, M.S., Chornik, B., Octadecylsilane-Modified Silicas Prepared by Grafting and Sol-Gel Methods, *J. Electron Spectroscopy and Related Phenomena*, 156-158, 413-420, **2007**.

25. Brambilla, R., Pires, G.P., dos Santos, J.H.Z., Lacherda-Miranda, M.S., Octadecylsilane Hibrid Silicas Prepared by the Sol-Gel Method: Morphological and Textural Aspects, *J. Coll. Int. Sci.,* 312, 326-332, **2007**.

26. Stevenson, F.J., Humus chemistry: genesis, composition, reaction, *John Wiley and Sons Inc.,* **1994**.

27. Sándor, M., Nistor, C.L., Szalontai, G., Stoica, R., Nicolae, C.A., Alexandrescu, E., Fazakas, J., Oancea, F., Donescu, D., Aminopropyl-Silica Hybrid Particles as Supports for Humic Acids Immobilization, *Materials,* 9, 34, **2016**.

28. Nistor, C.L., Donescu, D., Perichaud, A., Ballout, W., Ghiurea, M., Microencapsulation of an acrylate monomer in silica particles by sol-gel process*, J. Sol-Gel Sci. Technol.,* 57, 2, 164-171, **2011**.

29. Sándor, M., Nistor, C.I., Petcu, C., Purcar, V., Vuluga, M., Niţu, S., Trică, B., Donescu, D., Oxidative Degradation of Polyether Polyol - Silica Hybrids Prepared by Sol-Gel Process, *Revista de Chimie*, 67, 10, **2016**.

30. Purcar, V., Donescu, D., Ghiurea, M., Serban, S., Petcu, C., Pagnier, T., Podina, C., The effect of different cross-linking agents on the properties of hybrid films, *Optoelectron. Adv. Mat.,* 3, 3, 204-208, **2009**.

Scientific papers and communications

Articles published in ISI journals

Mónika Sándor, Cristina Lavinia Nistor, Gábor Szalontai, Rusandica Stoica, Cristian Andi Nicolae, Elvira Alexandrescu, József Fazakas, Florin Oancea, Dan Donescu, *Aminopropyl-Silica Hybrid Particles as Supports for Humic Acids Immobilization*, Materials, **2016**, 9, 34, (impact factor: 2.651);

Mónika Sándor, Cristina Lavinia Nistor, Cristian Petcu, Violeta Purcar, Mircea Vuluga, Sabina Niţu, Bogdan Trică, Dan Donescu, *Oxidative Degradation of Polyether Polyol - Silica Hybrids Prepared by Sol-Gel Process*, Revista de Chimie, **2016**, 67, 10, (impact factor: 0.81)**;**

Oral presentations

Sándor Mónika, Cristina Lavinia Nistor, Violeta Purcar, Szalontai Gábor, Rusandica Stoica, Szőke Anna-Mária, Dan Donescu, Fazakas József, *Synthesis of epoxysilane functionalized silica supports for humic acids immobilization*, Priorităţile chimiei pentru o dezvoltare durabilă, PRIOCHEM, Ediţia a X-a, Bucureşti, 30-31 octombrie **2014**;

Sándor Mónika, Fazakas József, Bartalis Ildikó, Szőke Anna Mária, *Chemical characterization of peat from Comandău and its alkaline extracts*, International Conference NATURA – ECON 4, Environmental Dynamics under the Impact of Economic Trends – Realities and Perspectives, Saint George, 7th March **2014**;

Poster

Sándor Mónika, Cristina Lavinia Nistor, Violeta Purcar, József Fazakas, Cristian Petcu, Cătălin-Ilie Spătaru, Marius Ghiurea, Raluca Ianchiş, Raluca Şomoghi, Dan Donescu *Preparation of aminopropyl hybrid silicas by the sol-gel method for immobilizing humic acids*, The XXXIII-rd Romanian Chemistry Conference, Călimăneşti-Căciulata, 01-03 October **2014**;