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Complete List of Authors:	El hadad, Amir; Centro Nacional de Investigaciones Metalurgicas (CSIC) Carbonell, Diogenes; Universidad Carlos III de Madrid, Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química Barranco, Violeta; Instituto de Ciencia de Materiales de Madrid (CSIC) Jiménez-Morales, Antonia; Universidad Carlos III de Madrid, Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química Casal, Blanca; Centro Nacional de Investigaciones Metalurgicas (CSIC) Galvan, Juan; Centro Nacional de Investigaciones Metalurgicas (CSIC)
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Preparation of Sol-Gel Hybrid Materials from γ-Methacryloxypropyltrimethoxysilane and Tetramethyl Orthosilicate: Study of the Hydrolysis and Condensation Reactions

A. A. El hadad[1], D. Carbonell[2], V. Barranco[3], A. Jiménez-Morales[2], B. Casal[1], J.C. Galván[1]

[1]Centro Nacional de Investigaciones Metalúrgicas (CSIC), Madrid, Spain,
[2]Universidad Carlos III de Madrid. Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química. (Madrid), Spain.
[3]Instituto de Ciencia de Materiales de Madrid (CSIC), Madrid, Spain.
e-mails: amirelhadad@cenim.csic.es, jcgalvan@cenim.csic.es

Abstract. Organic-inorganic hybrid materials suitable for the development of sol-gel coatings for metallic surfaces were prepared by hydrolysis and condensation of γ-methacryloxypropyltrimethoxysilane (MAPTMS) and tetramethyl orthosilicate (TMOS). The hydrolysis of MAPTMS/TMOS was carried out in an ethanol/water solution. The prehydrolysis stage of MAPTMS/TMOS system was monitored by Fourier Transformer Infrared Spectroscopy (FTIR) and liquid-state ^{29}Si and ^{13}C Nuclear Magnetic Resonance (^{29}Si and ^{13}C NMR). FTIR analysis indicated that the hydrolysis of MAPTMS/TMOS was accomplished as far as the (Si-OMe) band corresponds to unhydrolyzed silane disappeared. The concentration of the alkoxy groups and the extent of self-condensation of mono-, di-, and tri-substituted siloxanes (T species) in the sol were estimated by using liquid-state ^{29}Si NMR spectroscopy. The hydrolysis of the prepared sol was also evaluated by liquid state ^{13}C NMR spectroscopy. The results indicated that under the adopted synthesis strategy conditions, the hydrolysis process require four hours to be completed.

Keywords: sol-gel; silica; organic-inorganic materials; organopolysiloxane precursors; Si-29 and C-13 NMR; FTIR; structural characterization.

INTRODUCTION

The interest in developing novel organic-inorganic hybrid coatings in recent years is due to the unique properties derived from combining inorganic and organic components into a single system [1-7]. Inorganic and organic-inorganic sol-gel materials have many applications in diverse fields such optics, electronics, ionics, mechanics, energy, environment and biology [8,9], separation, catalysis and sensing

[10-15], electrochemistry [16-24], functional smart materials and corrosion protection coatings [8,9,25,26] or biomaterials and biomedical applications [9,27-30]. The sol-gel route, originally directed towards the synthesis of purely inorganic materials, is increasingly being extended to the preparation of organic-inorganic hybrid materials. The organic-inorganic hybrids combine the desirable properties of organic polymers (toughness, elasticity) with those of inorganic solids (hardness, chemical resistance). The sol-gel method as a materials processing technique has attracted intense and growing interest of the researchers because of its advantages over the other traditional preparation methods. This route enables the obtaining of high reactivity, better purity, avoidance of corrosive by products, improved control of the product structure and provides an easy, cost-effective and excellent way to incorporate inorganic compounds into an organic one [31-33]. The organic-inorganic hybrid materials can be easily prepared at room temperature by hydrolysis and condensation of metal alkoxides of the type $M(OR)_n$, where M is Si, Ti, Al, Sn, Zr, etc. This method comprises a chemical synthesis of materials having an oxide backbone and an additional organic component as a network former. Starting from hydrolyzable molecular compounds, such as alkoxy compounds of silicon, for instance tetramethyl orthosilicate (TMOS), the hydrolysis and condensation is induced by addition of water and a catalyst giving to the formation of an inorganic silica network. The organic silane precursor, for instance γ-methacryloxypropyltrimethoxysilane (MAPTMS), contains organic groups which act as network modifiers. Due to the presence of these modifiers, the final silicon network gains different properties (e.g. hydrophobicity, flexibility) depending on the nature of the organic group used [34]. The hydrolyzed Si-OH silanol groups are able to react with hydroxyl groups present on inorganic or metal surfaces, to form hydrogen bonds [35,36], followed by condensation to form oxane bonds [37,38]. Figure 1 shows a simplify view of the cascade reactions of hydrolytic deposition of silanes on inorganic or metal surfaces.

The excess Si-OH groups adsorbed on the surface can also condense among themselves to form Si-O-Si siloxane films [39]. Sol-gel coatings based on siloxane bonded units can be prepared starting from an organic-inorganic hybrid system. Thus the co-hydrolysis and polycondensation of the MAPTMS and TMOS mixture produce a polymeric structure (Figure 2), exhibiting properties of chemical compatibility and flexibility able to accommodate other species, as selected ionophores or corrosion inhibitors, without

showing phase segregation neither cracking processes. We have used these precursors for multifunctional purposes, to develop electrode-membranes [40,41], ion selective sensors [42,43] and self-repairing coatings for delaying the corrosion advance in metals [44].

The aim of the current paper has been to study the structural changes which take place during the hydrolysis and condensation processes of a MAPTMS/TMOS solution after the addition of water and ethanol. FTIR and liquid-state ^{29}Si and ^{13}C NMR have been applied for this purpose.

MATERIALS AND METHODS

Sol preparation

As described in detail elsewhere [42-44], sols were prepared starting from a mixture of 4 mol of γ-methacryloxypropyltrimethoxysilane (MAPTMS, Aldrich) and 1 mol of tetramethoxysilane (TMOS, Fluka). Ethanol (C_2H_5OH, 99.8%) and water were added with the molar ratio silane/water/methanol of 1/3/3. The resulting sol solution was completely transparent and without phase separation.

Fourier Transforms Infrared Spectrometer (FTIR).

The prepared sol samples were analyzed by FTIR spectral analysis. Each sample was prepared by mixing about 0.5 ml of sol with 200 mg of CSI, which was subsequently pressed into pellet in an evacuated die. All the spectra were measured by using a Nicolet Magna 550 infrared spectrometer at room temperature, which covers the wavenumber range of 4000-400 cm^{-1}.

Liquid-State Nuclear Magnetic Resonance (NMR).

^{29}Si and ^{13}C NMR spectra of the liquid samples were recorded at 79.49 and 100.62 MHz respectively, in a Bruker AVANCE-400 spectrometer. The external magnetic field was 9.4 Tesla. The single pulse NMR spectra were obtained after excitations with a π/2 pulse length of 6μs, for ^{29}Si and intervals between successive accumulations (recycle delay) of 5s for each type of signal. NMR spectra were registered for ^{13}C with a π/2 pulse length of 5μs and a recycle delay of 10s. The number of scans was 1600 in the case of ^{29}Si and 128 for ^{13}C. The ^{29}Si and ^{13}C chemical shift values are given relative to $Si(CH_3)_4$. The

deconvolutions of the NMR spectra were carried out with the WINFIT program so that the different components, and their contributions, could be determined.

RESULTS AND DISCUSSION

The reaction between silanes species in liquid media occurs, in general, by sol-gel process in which hydrolysis and condensation of the silane groups take place. In particular by mixing the two precursors (MAPTMS/TMOS) with H_2O/ethanol at ambient temperature, the hydrolysis taking place in the solution must be considered [45].

In this sense, FTIR is a rapid, nondestructive and sensitive analytical method for identifying functional groups present. The FTIR spectrum of the MAPTMS/TMOS upon mixing with EtOH/H_2O solvent system can be seen in Figure 3. The corresponding band assignments are present in Table1. The absorption bands around 2950 and 2840 cm^{-1} are attributed to stretching vibrations of C-H bonds in alkyl and methoxy groups, respectively [46]. The band close to 1720 cm^{-1} is associated to the stretching vibrations of C=O carbonyl groups of MAPTMS, while that one at 1640 cm^{-1} is attributed to C=C groups of the methacrylate groups from the MAPTMS precursor [46-48].

The bands at 1450 and 1150 cm^{-1} are attributed to deformation vibrations of C–H in CH_2 and CH_3 bonds [49,50]. The asymmetric and symmetric stretching vibrations of C-O of C-O-C bonds are attributed to bands at 1320 and 1300 cm^{-1}, respectively [49]. Finally, the bands at 941 and 822 cm^{-1} are assigned to the C=C vibrations of the C=C-C=O group, while that assigned to C-C-O skeleton vibration for pure ethanol appear at 1090 cm^{-1} [50]. All those bands (except the one at 2840 cm^{-1}) are related with the non-hydrolysable part of the MAPTMS-TMOS mixture, and should appear in the FTIR spectra carried out after the hydrolysis process.

The band at 1080 cm^{-1} is attributed to stretching vibrations of Si-O-C bonds. Other authors have also made the same attribution in different silanes [51,52]. This band is the one that expected to be broken during the hydrolysis process. Presence of the very little bands assigned to Si-O-Si bonds at 980 cm^{-1}

indicates that certain condensation of the silane chains has taken place immediately upon mixing [53]. These bands prove the existence of condensation phenomena together with the hydrolysis one.

The FTIR spectra of the MAPTMS/TMOS aqueous mixture are shown in Figure 4, for hydrolysis time varying from 15 minutes up to 3.5 h. In these spectra it is clearly observed that the FTIR spectrum of 3.5 h spectrum is very similar to that after 1 minute of mixing (Figure 3), which would indicate the incomplete hydrolysis of the mixture.

As the hydrolysis time increases, 4 hours of hydrolysis, the spectra change substantially (Figure 5A). The band at 2841 cm^{-1}, associated to the methoxy group, which appeared upon mixing (Figure 3), disappears for hydrolysis times of four hours (Figure 5A). This allows establishing the beginning of optimal hydrolysis conditions at about 4 hours. The same happens with the asymmetric stretching vibration of the Si-O-C, which was appeared at 1080 cm^{-1} (Figure 3). This bond is the one that must be broken during the hydrolysis, and its absence in Figure 5A implies the end of the hydrolysis process [53]. This band disappeared and replaced by two bands corresponding to Si-O-Si results from the condensation process. Disappearance of the band of Si-O-CH_3 groups at 2840 cm^{-1} were also evidenced together with the increase of a broad band at 3420 cm^{-1}, assigned to OH groups from SiOH formed through hydrolysis [53]. Figure 5 shows that for the hydrolysis time of 8 up to 24 hours, the slight broadening of Si-O-Si bands results from a highly cross linked network mainly consisting of linear polysiloxanes with a mixture of small and long chains.

The NMR nuclear magnetic resonance is a useful tool to study the silane hydrolysis; the NMR relaxation time measurements are sensitive to short-range interactions and can be used to estimate the scale of miscibility of an organic-inorganic hybrid [54]. This is due to the good resolution and quantitative assignment of the NMR peaks of silane molecules in comparison with the FTIR analysis [55].

Liquid-state ^{29}Si and ^{13}C NMR have been applied to study the hydrolysis mechanism of the MAPTMS/TMOS mixture in EtOH-H_2O solution. In the ^{29}Si NMR spectroscopy, the chemical shift of silicon is determined by the chemical nature of their neighbours, namely T, and Q structures [56].

A Q species is one in which the Si atom is capable of producing four siloxane bonds, results from TMOS precursor, whereas a T can only achieve three siloxane bonds and results from MAPTMS [31]. According to the nomenclature, four T signals of different nature can be present (T^n, where n=0; 1; 2; or 3, respectively) [32]. Figure 6 shows a achematic representation of T^n silane structures. T^0 appears in a spectral range from -37 to -39 ppm which is assigned to $RSi(OCH_3)_3$ unhydrolyzed species from MAPTMS. T^1 occurs in the range defined between -46 to -48 ppm, assigned to condensed silicon units bearing only one bridging oxygen atom (Si-O-Si), T^2 is defined in the spectral range defined between −53 to −57 ppm which is assigned to doubly condensed silicon centres (two bridging oxygen atoms), and T^3 is defined into the −61 to −66 ppm range, fully condensed silicon units (three bridging oxygen atom) as sketched in the Figure 6 [56].

The ^{29}Si spectra of MAPTMS /TMOS in EtOH-H_2O solution are shown in Figure 7. Upon mixing of the two precursors (Figure 7A), the $RSi(OCH_3)_3$ species from non-hydrolyzed MAPTMS (T^0 units) give a well detectable singlet signal at -42 ppm. The appearance of mono-, di-, and tri-substituted siloxanes T species (T^1 units at -50 ppm, T^2 units at -59 ppm, and T^3 units between -68 and -71 ppm) is a result of the self condensation. These observations are in agreement with the FTIR results which showed the presence of condensed siloxane species at 980 cm^{-1} upon mixing of the two precursors, indicated by presence of the Si-O-Si band (Figure 3). The $Si(OCH_3)_4$ unhydrolyzed species from TMOS were not detected in the ^{29}Si spectra upon mixing of the two precursors with H_2O/ethanol and this because TMOS was used in little amount and so has been hydrolyzed upon mixing.

After 1 hour of the reactive mixing, both the T^1 at 49.81 ppm and T^2 at 58 became clear and dominate the entire spectrum which indicates the progress of the hydrolysis process (Figure 7B). Also the T^3 of hydrolyzed MAPTMS and Q^2 and Q^3 of hydrolyzed TMOS appear as very small signals at 67.55, 91.78 and 101.66 ppm, respectively.

After 2 hours of hydrolysis and up to 3 hours (Figures 7C and 7D), there is not a significant change between these spectra and that of after 1 hour and the concentrations of condensed T^2 and T^1 species units remain constant (Figure 7B).

After 4 hours of hydrolysis, the T species in the form of T^1, T^2 and T^3 at -50, -58 and -68 ppm dominate the entire spectrum (Figure 7E). These results shed light upon two important observations which indicate that 4 hours were enough for the hydrolysis of the of MAPTMS/TMOS mixture, in a similar way as the FTIR spectra has indicated. It can observe:

- The non existence of unhydrolyzed TMOS, (Si $(OCH_3)_4$), as it hydrolyzed very rapidly.
- The disappearance of the signal T^0 corresponding to the initial unhydrloyzed MAPTMS (Figure 7A).
- The appearance of the signal T^3, which correspond fully to condensed silicon units with three siloxane bonds (three bridging oxygen atom) dominated all the spectrum of 4 hours.

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The ^{29}Si NMR spectra provide the proportions of T^n species (n=1; 2; or 3), where T represents a Si atom oxygen bridged to another Si atoms. These allowed the quantification of the crosslinking degree within the silicate network. The T^1, T^2 and T^3 units arose from the self-condensation reactions only. The T^1 units represented dimers or chain ends. The T^2 were associated with the linear siloxane sequences, and the T^3 units witnessed about the appearance of three-dimensional siloxane networks. In fact, the non-reacted silane molecules (T^0 units) from MAPTMS gave a well detectable singlet signal at –42 ppm (Figure 7A). This singlet disappeared from the spectrum after 1 hours of reactive mixing, indicating beginning of hydrolysis reaction.

As it was expected from the FTIR results, the maximum of self-condensed products was observed after 4 hours of reaction. The proportions of the T species in each hybrid system quoted in Table 2 were obtained from deconvolution of the ^{29}Si NMR spectra with the WINFIT software. The spectra were deconvolved into individual Gaussian line shapes, thus allowing a quantitative analysis of the spectra based on the peak areas of each species. From Figure 8, it can be seen that after 4 hours of hydrolysis the amount of T^3 silicon content increased while that of T^2 and T^3 silicon content decreased in the matrix of the Si-O-Si structure. That the hydrolysis was accompanied by a condensation reaction among the silanol groups to give oligomeric structures.

The ^{13}C NMR spectra of MAPTMS/TMOS in EtOH-H_2O is shown in Figures 9 and 10. This mixture was hydrolyzed for 4 hours in EtOH-H_2O solution. In comparison with the ^{29}Si NMR spectra, the patterns of the ^{13}C NMR peak positions are significantly exhibiting multiple peaks. This suggests that there are several chemical compounds within the hybrid systems containing carbon-bonding structures. Peaks assignments for carbon-bonding types which can be attributed to the MAPTMS and TMOS precursors are given in Table 3. The peaks from TMOS and MAPTMS in the ^{13}C NMR spectra are in good agreement with earlier reports [57]. The hydrolysis of the MAPTMS/TMOS system was followed by the evolution of the peaks corresponding to the methyl groups attached to the silane and those liberated during the hydrolysis (CH_3-OH and CH_3-CH_2-OH).

Upon mixing of the two silane precursors with EtOH-H_2O solution, the peaks at 17.45 and 57.29 ppm are from ethoxy groups of ethanol and to CH_3-C of MAPTMS [58] (Figures 9A and 10A). The peaks at 48.97 are ascribed to unhydrolyzed CH_3-O-Si units of MAPTMS and TMOS. The peak at 67.10 ppm is attributable to CH_2-CH_2-O units of MAPTMS while that appear at 22.47 ppm are due to CH_2-CH_2-Si units of the same precursor. Finally, the peak at 9.18 ppm are attributed to Si-C of MAPTMS.

Up to 2 hour of reaction, no changes can be detected (Figures 9B-9C and Figures 10B-10C). Thus the spectrum exhibits the same peaks corresponding to the carbon within the hybrid systems containing carbon-bonding structures. After 3 hours of hydrolysis, the spectrum exhibit significant changes (Figures 9D and 10D). The peak that appear at 49 ppm corresponds to the release of methanol as a result of beginng of condensation process. The emergence of this peak indicates the hydrolysis of the methoxy group in (H_3C-O-Si) of both precursors. The hydrolysis of methoxy groups caused by water in ethanol, contributed to the yielding of methanol as a reaction product that it is seen in the liquid-state ^{13}C NMR spectra [59]:

$$\equiv Si - OCH_3 + H_2O \xrightarrow{CH_3CH_2OH} \equiv Si - OH + CH_3OH$$

At the same time, during the hydrolysis of TMOS in ethanol, methoxy groups of TMOS are exchanged for alkoxy groups. This reaction is an equilibrium reaction. Almost all of methoxy groups are exchanged for ethoxy groups. This give a well developed band that newly emerged at 7.62 and 57.26 ppm in the

spectrum of three hours hydrolysis (Figures 9D and 10D), corresponding to Si-O-CH_2-CH_3 units and methanol is released into the solution following the next reaction.

After 4 hours of hydrolysis it takes place, the disappearance of the methoxy groups of the initial silanes at 48.97 ppm and the concomitant formation of free methanol, as indicated by the peak growing at 49 ppm of hydrolyzed mixture [60] (Figure 10E). Thus the the disappearance of the resonances assigned to the CH_3-O-Si group is accompanied by the increase of the CH_3-OH signal. All these facts can confirm that four hours are enough for the hydrolysis reactions to be completed.These results indicated that the hydrolyzable Si-O-CH_3 groups of both precursors were hydrolyzed and forming silanol groups that could derive in Si-O-Si bonds due to subsequent condensation.This agrees well with the results obtained from ^{29}Si NMR, that showed that the hydrolysis was accompanied by a condensation reaction among the silanol groups to give oligomeric structures. The evidence of the presence of such structures was provided by the broadening of the different peaks in the ^{13}C NMR spectra.

CONCLUSIONS

The sol-gel reaction of the MAPTMS/TMOS system in EtOH/H_2O solution was studied by FTIR and NMR. The aim of the study was to optimize the pre-hydrolysis times of both silanes and consequently their use as precursors for hybrid materials. The early step of the condensation process was studied by collecting ^{29}Si NMR spectra and the quantitative analysis of the condensed species was calculated in terms of T^1, T^2 and T^3 silicon units. It could be concluded that the hydrolysis of the two silane precursors under the adopted synthesis strategy conditions is completed after approximately, four hours at room temperature. The quantitative analysis of the NMR indicates that presence of self-condensation species after mixing of the two precursors which react betwween them as the time proceeds results in progress of the hydrolysis process. the hydrolysis was accompanied by a condensation reaction among the silanol groups to give oligomeric structures.

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LIST OF FIGURES

Table 1. Assignment of the FTIR peaks shown in Figure 3

Wavenumber (cm^{-1})	Assignment	References
2950	$\nu_{as\ C\text{-}H}$ (CH_3)	[46]
2840	$\nu_{sC\text{-}H}$ (O-CH_3)	[46]
1720	$\nu_{s\ C=O}$ (methacryloxy group)	[46-48]
1640	$\nu_{C=C}$ (methacryloxy group)	[46-48]
1450	δ_{CH2} (Si-R organic group)	[49,50]
1320	$\nu_{as\ C\text{-}O}$ (C–O–C bonds)	[49]
1300	$\nu_{s\ C\text{-}O}$ (C–O–C bonds)	[49]
1080	$\nu_{as\ Si\text{–}O}$ (Si-O-CH_3)	[51]
1187	ν_{as} (Si–O–Si)	[53]
1085	ν_s(Si–O–Si)	[53]
3100-3600	$\nu_{O\text{-}H}$ (Si-OH)	[53]

s: symmetric; as: asymmetric

Table 2. Relative proportions of T and Q species in the organic–inorganic hybrid materials from the liquid-state ^{29}Si NMR spectra in Figure 7

Time in M	Proportions [a] (%)						Relative[b] proportions (%)				Relative proportions[c] (%)		Ratio[d] (%)	
	T^0	T^1	T^2	T^3	Q^2	Q^3	T^0	T^1	T^2	T^3	Q^2	Q^3	T^n	Q^n
1	47.66	10.87	9.64	31.83	0	0	47.66	10.87	9.64	31.83	-	-	1	-
60	-	40.28	38.48	11.08	3.21	6.95	-	44.83	42.83	12.34	31.5	68.5	89.8	10.2
120	-	41.38	36.80	7.83	6.52	7.47	-	48.11	42.78	9.11	46.6	53.4	86	14
180	-	50.41	35.35	4.45	4.2	5.59	-	55.88	39.18	4.93	42.90	57.1	90	10
240	-	9.91	35.56	54.53	-	-	-	9.91	35.56	54.53	-	-	1	-

[a] Proportions (%): these were calculated by the deconvolution technique. Error value assumed is ±1%.
[b] Relative proportions (%): (each T species/total T species) · 100%.
[c] Relative proportions (%): (each Q species/total Q species) · 100%.
[d] Ratio (%): Ti = {total T species/(T species + Q species)} · 100%, Qj = {total Q species/(T species + Q species)} · 100%.

Table 3. Peaks assignments of liquid-state ^{13}C NMR spectra of both MAPTMS and TMOS according to peaks detected in Figure 9

MAPTMS (Aldrich)		TMOS (Aldrich)		Ethanol	
Nature of carbons	Ass.(ppm)	**Nature of carbons**	Ass.(ppm)	**Nature of carbons**	Ass.(ppm)
CH_2--$\underline{C}H_2$-O	67.10	$\underline{C}H_3$-O-Si	48.97	CH_2-OH	57.29
CH_3-O-Si	48.97			$\underline{C}H_3$ -CH_2	17.45
CH_2-CH_2-Si	22.47				
$\underline{C}H_3$-C	17.45				
CH_2-Si	9.18				

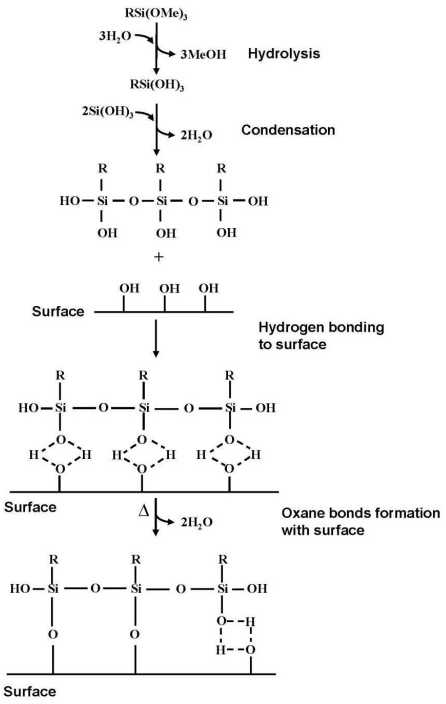

Figure 1. Reaction and bonding mechanism of alkoxysilanes

210x297mm (200 x 200 DPI)

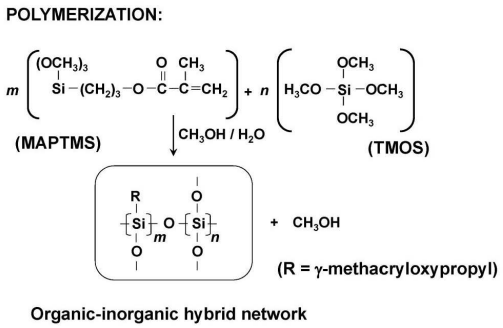

Figure 2. Schematic representation of the polymerization reaction of the MAPTMS and TMOS mixture producing a 3D organic-inorganic hybrid network

210x297mm (200 x 200 DPI)

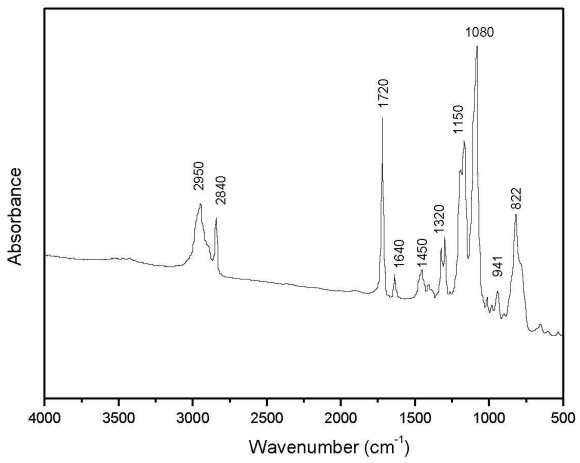

Figure 3. FTIR spectrum of the MAPTMS/TMOS mixture in EtOH-H_2O solvent system upon mixing

210x297mm (200 x 200 DPI)

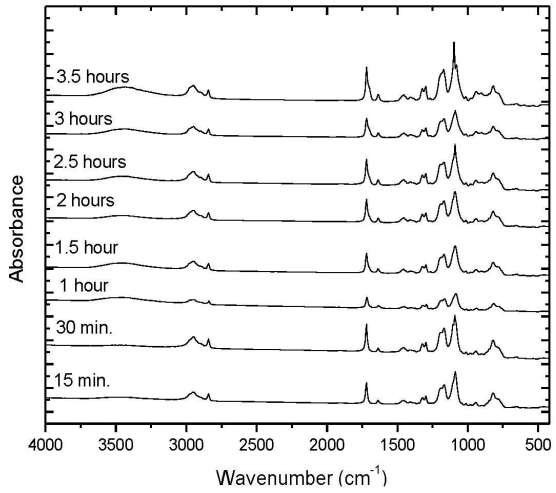

Figure 4. FTIR spectra of the MAPTMS/TMOS mixture in EtOH/H_2O solvent system. Hydrolysis time up to three hours and a half

210x297mm (200 x 200 DPI)

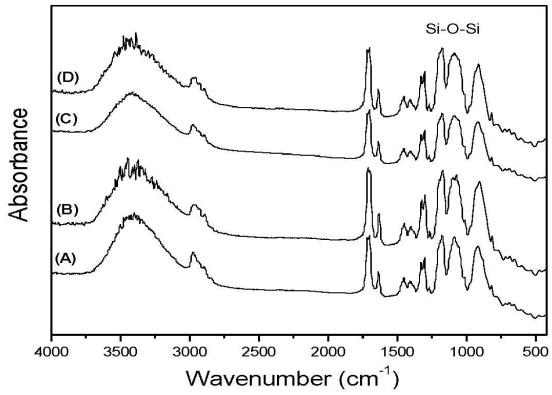

Figure 5. FTIR spectra of MAPTMS/TMOS mixture in EtOH/H_2O solvent system. Hydrolysis time up to twenty four hours. (A) 4 hours (B) 8 hour. (C) 12 hours (D) 24 hours

210x297mm (200 x 200 DPI)

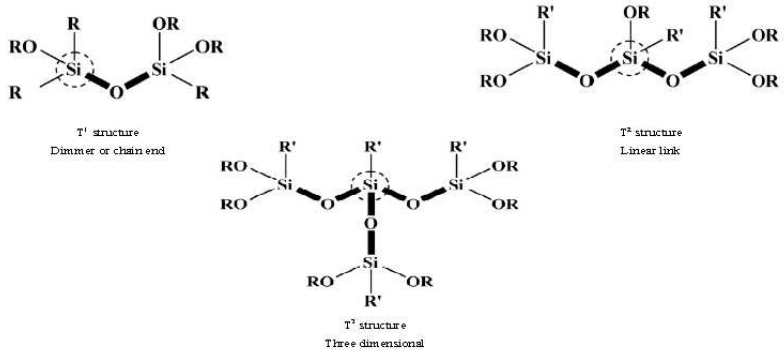

Figure 6. Schematic representation of T^n silane structures (n=1, 2, or 3)

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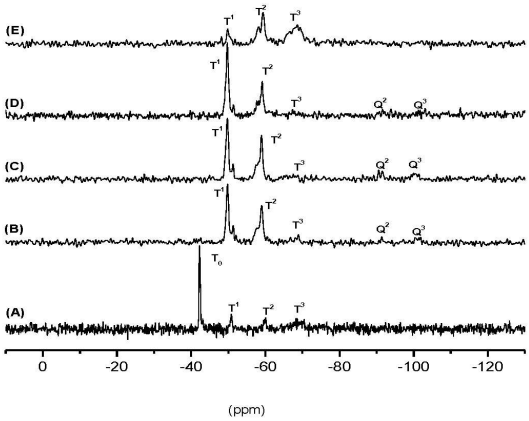

Figure 7. Liquid state ^{29}Si NMR spectra of MAPTMS/MOS mixture in EtOH-H_2O solvent system. (A) Upon mixing of MAPTMS and TMOS (B) After one hour. (C) after two hours (D) after three hours (E) after four hours

210x297mm (200 x 200 DPI)

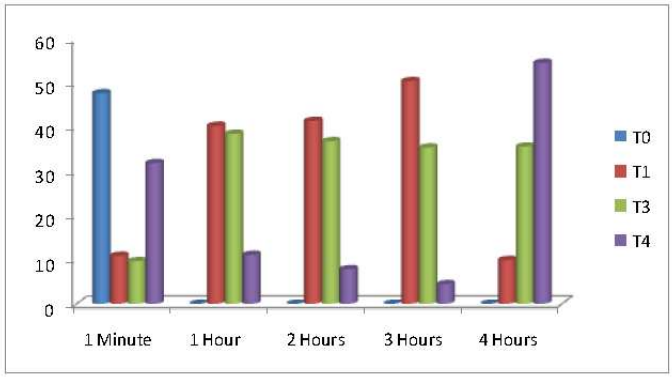

Figure 8. Relationship of the signals, for species T^0,T^1, T^2 and T^3 in the MAPTMS/TMOS hybrid

210x297mm (96 x 96 DPI)

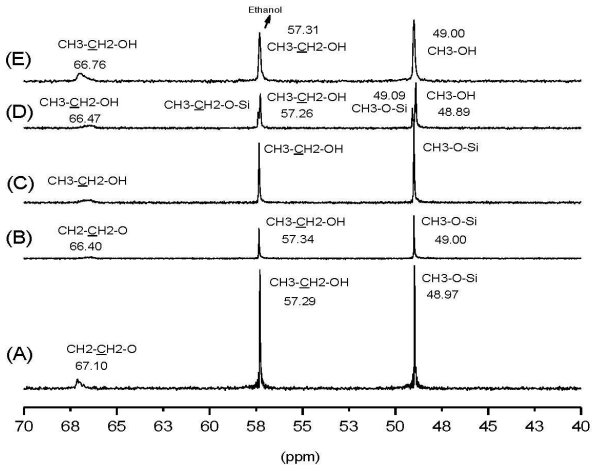

Figure 9. Liquid state ^{13}C NMR spectra (0-30 ppm range) of prehydrolyzed MAPTMS/TMOS mixture. (A) Upon mixing of MAPTMS and TMOS, (B) after 1 hour, (C) after 2 hours, (D) after 3 hours and, (E) after 4 hours

210x297mm (200 x 200 DPI)

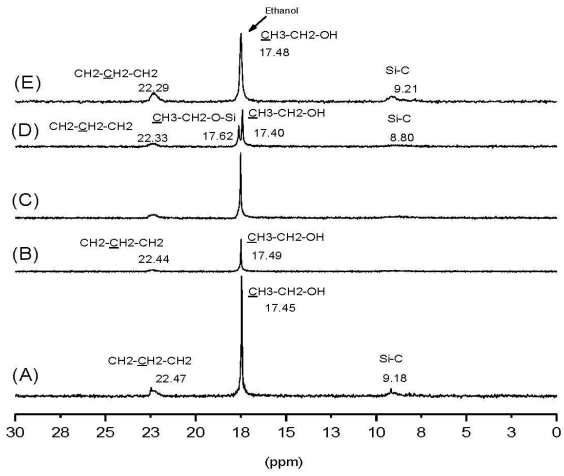

Figure 10. Liquid state ^{13}C NMR spectra (40-70 ppm range) of the prehydrolyzed MAPTMS/TMOS mixture. (A) Upon mixing of MAPTMS and TMOS, (B) after 1 hour, (C) after 2 hours, (D) after 3 hours and, (E) after 4 hours

210x297mm (200 x 200 DPI)