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Article

Sol Gel Derived Silica Matrix. Solution Concentration of the Supplied Catalyst Influence upon Nanoporous Material Morpho-Textural Properties

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ABSTRACT

Template free, base catalysed sol-gel route (Stöber method) and low power sonic-activated sol-gel process (20 kHz ultrasonic bath) were used to obtain two series of samples. The influence of the concentration of the supplying ammonia solution upon the silica sols stability and solid products properties was followed. The reactants molar ratio TEOS: H_2O: ETOH: NH_3 of 1: 25: 20: 0.2 was rigorously kept constant. We have examined the influence of adding the ammonia solutions of different concentrations, specifically: 25% NH_3, 12% NH_3, 6% NH_3, and 3% NH_3. Either relatively stable colloidal suspensions or precipitates were obtained. The silica sols stability was related to the evolution of the turbidity over time. The resulted solid materials, xerogel's and sonogel's texture and morphology have been studied by using BET, SEM techniques. FT-IR was used to exhibit the main silica bonds. It was observed that by supplying base catalyst of variable concentrations, by changing initial pH of the process, it makes a difference concerning silica suspension behaviour and also in silica particle morphology. The used variable produced distinct effects upon both classic process and resulted xerogels, and sonoactivated sol-gel process and resulted sonogels. For all concentrations of ammonia solution, by classic sol-gel process, silica precipitates were obtained, and under ultrasonic field action, relatively stable translucent silica colloids resulted.

Keywords: sol-gel, Stöber process, turbidity, suspension

1. INTRODUCTION

The sol-gel process has been widely used as a very flexible route for the fabrication of silica gel powders in order to produce new porous nanomaterials with well-defined structures, complex shapes and high purity. The sol-gel process was described as relatively simple way, assuming low cost, saving energy, allows the control of the distribution of the component molecules in silica condensed polymers. These materials synthesized by sol-gel method were used for medical science in drug delivery systems [1]. The structural properties of these materials synthesized depend on various experimental parameters (effect of catalyst concentration, pH, etc.). The catalyst concentration and its influence on the silica sols and on the properties of SiO_2 particles have been evaluated for a long time. Stöber et al. [2] reported a pioneering method for synthesizing silica nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as catalyst. They observed that the silica particles are produced at high concentration of ammonia and small, poly-disperse silica are obtained at low ammonia concentration. Rao and Parvathy [3] have specified that silica gels can only be obtained at 0.01 N concentration of catalyst, while at concentrations higher than 0.01 N, only turbid and opaque colloid solutions (sols) arise. This result may be explained by the interaction of TEOS with the catalyst (ammonia) strongly influenced by synthesis and processing parameters. Fardad [4] studied the role of different catalysts, including ammonia at two different concentrations of 0.01M and 0.001M. At these concentrations the silica sol became translucent and large particles were formed at the end. Ibrahim and al. [5] prepared the silica spherical particles in which was studied the effect of catalyst concentration (NH_3) on the silica particles size. They observed that the silica particles increasing with catalyst (NH_3) concentration in the range 0.11÷0.3 M. Sumathi and al. [6] synthesizing the silica spherical particles, by using sol-gel method. They investigated the role of catalyst concentration on the small size of silica particles at low concentrations. With the increase in the amount of NH_3, the size of particles gradually increased and produces irregular spherical particles with high aggregation effect.

It has to be clearly explained that to our best knowledge, all previously reported experiments dealing with the influence of pH or catalyst concentration on the sol-gel process and/or upon the resulted nanomaterials properties, were based on the study of sample series prepared at alcoxide precursor (TEOS): catalyst (NH_3) variable molar ratio.

In the present work has been described the influence of catalyst, NH_3 (by measuring pH) on the silica suspension and silica structural parameters (surface area, porosity, shape and size) following a different rule. Specifically, it was established the reaction mixture molar ratios, including alcoxide: NH_3 one that was kept constant in all samples. Stable (no gelling) silica sols and solid silica particles were obtained under different basic and stirring conditions.

The aim of paper was the synthesis and characterization of silica particles and colloids by sol-gel process non-assisted (mechanic stirring) and assisted by ultrasonic field (20 kHz ultrasonic bath). Ammonia solution with different concentrations, obtained by successive dilutions, were supplied which clearly influenced the suspension stability and silica morphology. By only varying the concentration of catalyst added solution we can get the control on the silica hydrolysis and condensation process and therefore over structural properties of the synthesized silica. All the concentrations of ammonia mentioned in paper were calculated in relation to the total amount of water brought into the system that was kept rigorously constant. It has been noted once again, the molar ratio TEOS: H_2O: NH_3, for overall process, was also rigorously kept constant.

2. METHOD

Experimental Method

BET surface areas and BJH pore size were determined from N_2 adsorption/desorption isotherm at 77 K using a Quantachrome Nova 1200e instrument. Degassing of the samples in vacuum for 4 hours at room temperature (298 K) precede every measurement;

Pore volumes were calculated from the last point of adsorption isotherm; pore diameters were calculated by Barrett-Joyner-Halenda (BJH) method from the adsorption/desorption branches of the isotherms using a NovaWin software;

The morphological characterization of the samples was done by using Scanning Electron Microscopy (SEM). For SEM an INSPECT S (FEI Company, Holland) instrument has been used;

FT-IR spectra were carried out as KBr pellets, in the 4000-400 cm^{-1} range on JASCO 430 apparatus.

3. Results and Discussions

Silica nanoparticles were synthesized in two ways, following the Stöber process and keeping the same molar ratio of reactants TEOS: H_2O: ETOH: NH_3 1: 25: 20: 0.003 ***0.2***. For the first series, mechanical stirring route was used and xerogels were obtained. The second series were realized by sono-catalyzed sol-gel process, keeping all the process parameters at the same regime and sonogels were obtained. Total NH_3 amount in the reactants mixture was kept constant and ammonium supplied solutions concentrations were varied on the expenses of water amount calculated for a value of 25 (mole H_2O:mole TEOS).
The synthesis parameters are presented in the Table 1 and rigorously kept constant.

Table 1: The molar ratio of reactants TEOS: H_2O: ETOH: NH_3 1: 25: 20: 0.2

Samples		TEOS [Mol]	Water* [Mol]	ETOH [Mol]	NH_3 [mol]	NH_3 solution [%]
Xerogels	Sonogels					
S1P1	S2P1	1	25	20	0.2	25%
S1P2	S2P2	1	25	20	0.2	12%
S1P3	S2P3	1	25	20	0.2	6%
S1P4	S2P4	1	25	20	0.2	3%

*Total water amount was kept constant related to variable ammonium supplied solution concentrations

It was prepared two series of samples, each one being composed of four samples. For the first series (classic sol-gel route), the S1P1 sample was prepared by adding 0.23 ml solution of 25%NH_3. The second sample, S1P2, was prepared by adding 0.46 ml of solution 12%NH_3

and so forth, the following 2 samples, S1P3 and S1P4, were prepared by supplying further diluted ammonia solutions of 6%NH_3 and 3%NH_3 respectively.

The sonoactivated series of samples was prepared by following the same procedure except supplementary treatment in ultrasonic field in described conditions. For the second series (ultrasonic bath), the S2P1 sample was prepared by adding 0.23 mL solution of 25%NH_3. The following samples S2P2, S2P3 and S2P4 were made by successive dilutions of 12%NH_3, 6%NH_3 and 3%NH_3 supplying ammonia solution concentration. The way, in which synthesis has been achieved, amount of reactants, was revealed in the Table 2.

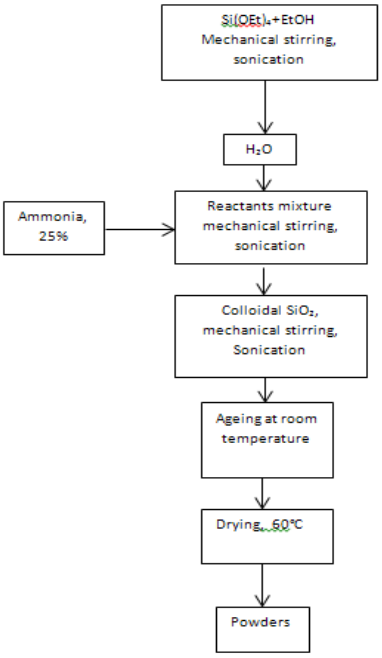
Table 2: The synthesis parameters

Samples		TEOS [mL]	Water [mL]	ETOH [mL]	NH_3 [mL]	*NH_3solution [%]	$pH_{NH3\ solution}$
Xerogels	Sonogels						
S1P1	S2P1	3.5	6.89	18.6	0.23	25%	12
S1P2	S2P2	3.5	6.60	18.6	0.45	12%	11
S1P3	S2P3	3.5	6.15	18.6	0.9	6%	10.5
S1P4	S2P4	3.5	5.25	18.6	1.8	3%	10.5

*NH_3 solutions added were diluted on account of water added to the system TEOS-H_2O-ETOH-NH_3

The main steps of xerogels and sonogels synthesis technology are presented in Figure 1.

Figure 1 Technological synthesis

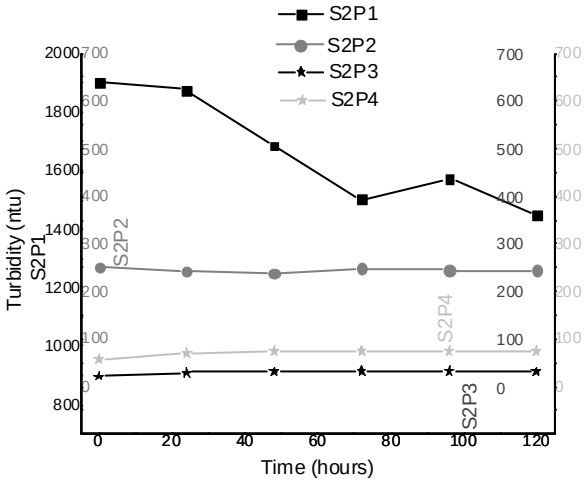


We systematically have examined the influence of adding the base solutions at different concentrations, specific, 25%, 12%, 6%, 3%NH_3, upon the silica sol stability and also upon

the resulted silica xerogel and sonogel samples properties. More or less stable colloidal suspensions and/or precipitates were obtained. The xerogels/sonogels turbidity was measured.

The sonogels kept their stability over the time. The evolution of sonogels stability was exhibited in Figure 2.

Figure 2 Turbidity evolutions over time



24 hours after synthesis, it could be observed that for the sample with the highest concentration of ammonia solution, S2P1 (25% NH_3), nucleation and growth phase occurred by Ostwald Ripening. After 72 hours the flocculation, the particles will be attracted by Van der Waals forces, aggregation begins. This was suggested that the colloidal system is an emulsion the droplets will coalescence, and also increasing the value of turbidity. The decreased value of turbidity after 96 hours indicated that deposition of particles occurred. The same phenomenon took place for the sample S2P2 (12%NH_3), nucleation (growth) – flocculation – aggregation – deposition. The smallest and constant values in time of the turbidity were for the samples treated with lower supplying NH_3 solution concentrations, namely S2P3 (6%NH_3) and S2P4 (3%NH_3), showed that particles deposition never occurred, remain translucent/transparent and kept the stability over the time.

The structural characterization of silica xerogels were carried out using BET [7] surface area analyser (Quantachrome Nova 1200e) at 77K. N_2 adsorption/desorption isotherms over a range of relative pressure P/P_0 from 0.05÷0.1 were collected for all samples. Specific surface areas were determined from the BET equation at a relative pressure range between 0.05÷0.1. The total pore volume was calculated from the last point of adsorption isotherm. Pore size was calculated with the equation (D) = $\frac{6}{S_{BET} \cdot d_{SiO_2}}$, where d_{SiO2}=2.2 g/cm^3 [8]. The N_2 adsorption/desorption isotherms are presented in Figure 3a) and Figure 3b).

Figure 3a) N_2 adsorption/desorption xerogel's isotherms

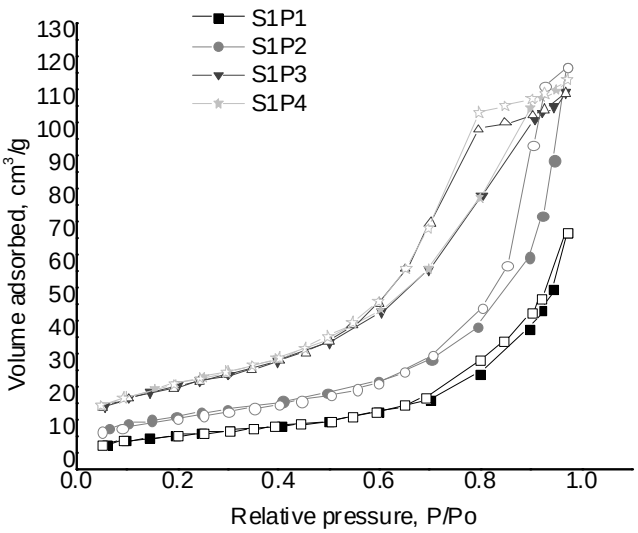
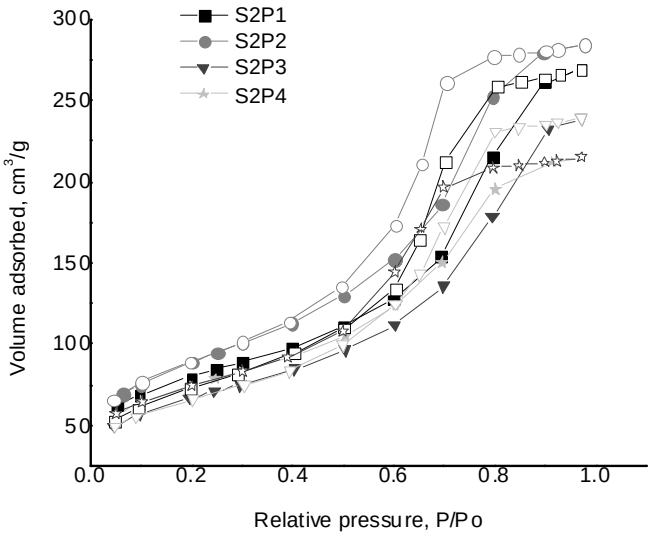


Figure 3b) N_2 adsorption/desorption sonogel's isotherms



Both silica series exhibited Type IV isotherm with H2 and H3 hysteresis loop according to IUPAC classification which is characteristic for mesoporous solids [9]. In Figure 3a) the adsorption/desorption isotherms for xerogels were presented. After BDDT classification [10], the N_2 adsorption/desorption isotherms were type IV, that are typically for mesoporous materials. The N_2 adsorption/desorption isotherms present different types of hysteresis loop, due to the capillary condensation taking place in the mesopores. The xerogels S1P1 (25% NH_3) and S1P2 (12% NH_3) indicate a type H3 hysteresis loop, according to IUPAC classification [9]. At the relative pressure range of 0.6 P/Po, the H3 hysteresis loop was attributed to the inter-particle porosity distance. Usually, these types of hysteresis loop owe

their shape to presence of aggregates, giving rise to slit-shaped pores [9]. The samples S1P3 (6%NH_3), S1P4 (3%NH_3) indicate a type H2 hysteresis loop which was explained as a consequence of the inter-connectivity of pores – "ink bottle" pores [11].

Figure 3b) shows the N_2 adsorption/desorption isotherm for the samples under ultrasonic field action. The N_2 adsorption/desorption isotherm shows a typical IUPAC type IV [9] pattern with sharp inflection of nitrogen adsorbed volume at P/P_0 about 0.4, with an H2 hysteresis loop [9], suggesting the existence of mesopores with an interconnected pores network of different shapes and sizes. From N_2 adsorption/desorption isotherms were derived the textural parameters of xerogels/sonogels. In Table 3 and Table 4 are presented the textural-parameters for xerogels and sonogels series.

Table 3 Xerogels texturals parameters

Xerogels	Pore diameter (BJH Ads.) [nm]	Pore diameter (BJH Des.) [nm]	Surface area (BET) [m^2/g]	Total pore volume [cm^3/g]	Particle size [nm]
S1P1(25%NH_3)	8.83	8.77	36	0.11	74
S1P2(12% NH_3)	6.15	17.92	56	0.18	48
S1P3(6% NH_3)	6.16	6.59	89	0.17	30
S1P4(3%NH_3)	6.14	6.55	92	0.18	29

Table 4: Sonogels texturals parameters

Sonogels	Pore diameter (BJH Ads.) [nm]	Pore diameter (BJH Des.) [nm]	Surface area (BET) [m^2/g]	Total pore volume [cm^3/g]	Particle size [nm]
S2P1(25%NH_3)	8.68	6.62	275	0.41	9.9
S2P2(12% NH_3)	8.74	6.65	314	0.44	8.6
S2P3(6% NH_3)	6.16	6.58	235	0.37	11.5
S2P4(3%NH_3)	6.14	5.68	257	0.33	10.5

Supplementary information on the effects of supplied ammonia solution concentration on the gels structure can be remarked from the pores size distribution. In figure 4a) and Figure 4b) are represented the pores size distributions for both series.

Figure 4a) Xerogels size distribution

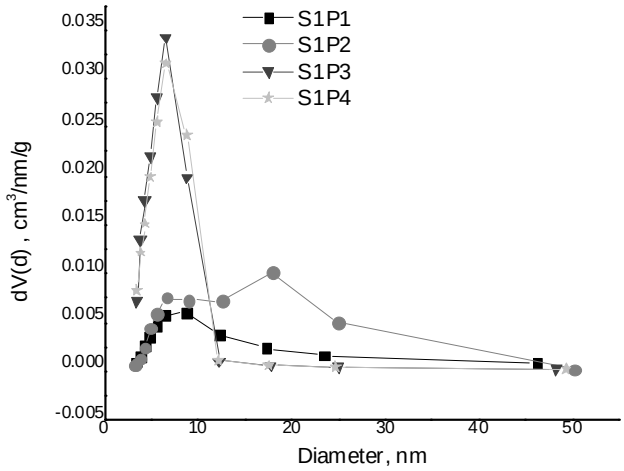
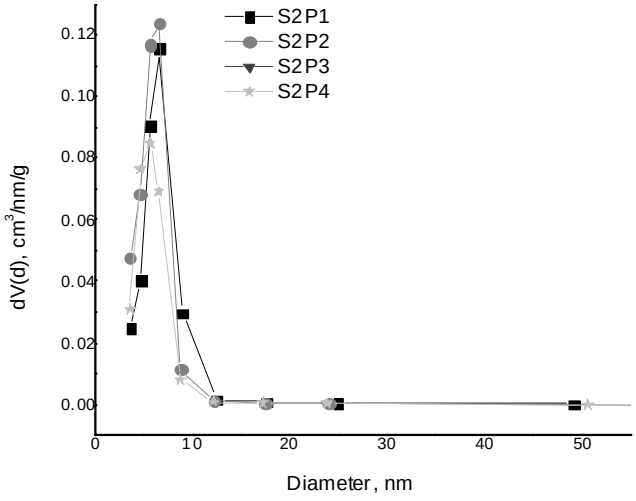


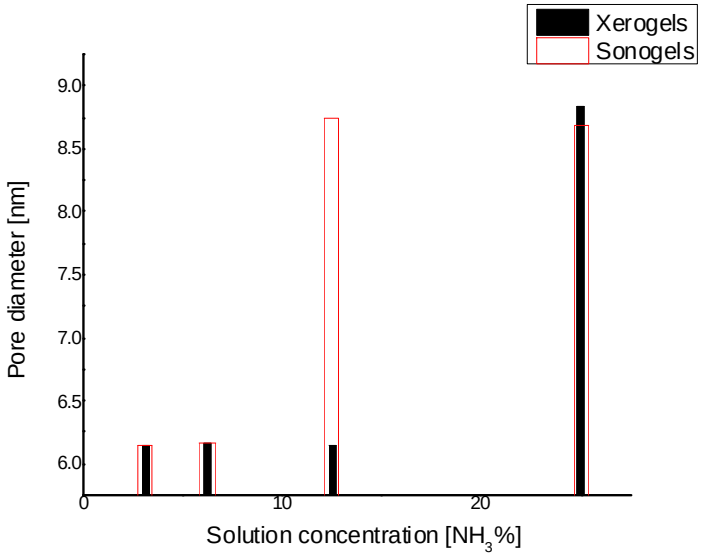
Figure 4b) Sonogels size distribution



From Figure 4a), the xerogels presented a large pore size distribution in the domain *2-50 nm* that was characteristic for mesoporous materials. Xerogels obtained by decreasing ammonia solution concentration, namely S1P1 and S1P2 exhibit a wide pore distribution related to xerogels with small concentration where the pore distribution was narrower, specifically the samples S1P3, S1P4 where the pore diameter was around of 7 nm). The sample S1P2 has a bimodal distribution with two maxim peaks around 7 nm and 20 nm.

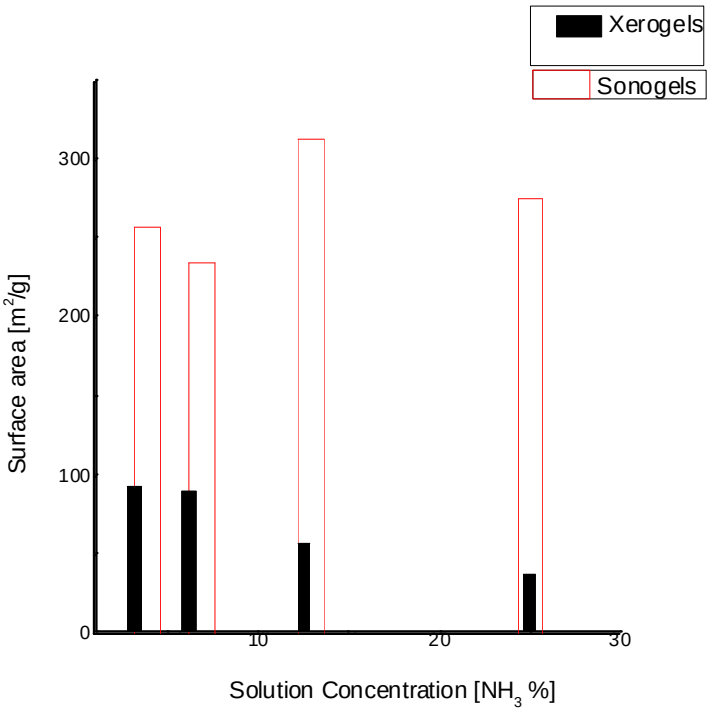
From Figure 4b) it can be seen that in the case of sonogels, the pore size distribution was narrower and centred in the domain 2-10 nm, where the most pores were found.
A correlation of textural parameters (pores diameter, surface area, and pores volume, particles size) was attempted with the concentration of ammonia solution. Figure 5 it showed the variation of pore diameter related to supplied NH_3 solution concentration for both series of xerogels/sonogels series.

Figure 5 Pore diameter related to ammonia solution



For both series, from adsorption/desorption isotherm it can be seen that by increasing the ammonia supplied solution concentration leads to the higher pore diameters. From desorption isotherm branch we can not have a clear orientation for xerogels because the sample S1P2 has an out of range value (12%S1P2 17.92 nm). From adsorption isotherm branch it can be seen that the pore diameter increase with supplying NH_3 solution concentration, the highest value was obtained for 25%S1P1 (~8.8 nm). It has to be noted that the average particle diameters of sonicated series are considerably smaller and they present a narrower distribution. The value of pore diameter for both series was 6-9 nm (from adsorption branch).
In Figure 6 was represented the surface area correlated with supplied ammonia solution for both xerogels/sonogels series.

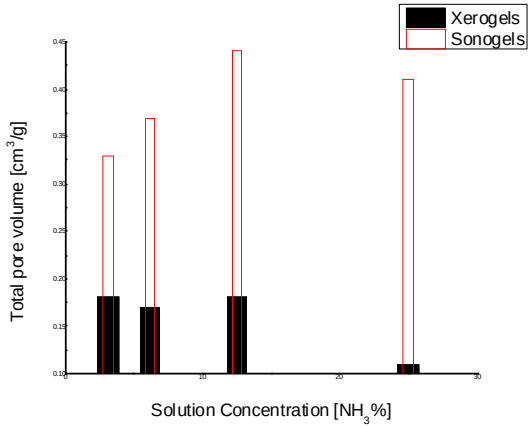
Figure 6 Surface area related to ammonia solution



From Figure 6, it can be seen that in the case of xerogels series, the highest surface area of 92 m^2/g, corresponding to the most diluted catalyst supplied solution, S1P4 (3% NH_3). Within the xerogel series, surface area presented a continuous increased tendency as supplied ammonia was more diluted. The sample S1P1 (25% NH_3) has the smallest surface area (36 m^2/g). In the case of the sonicated series, first of all, it was observed that surface areas significantly increased. By using supplied ammonia solution concentration of 12% NH_3, the highest surface area that was obtained, 314m^2/g.

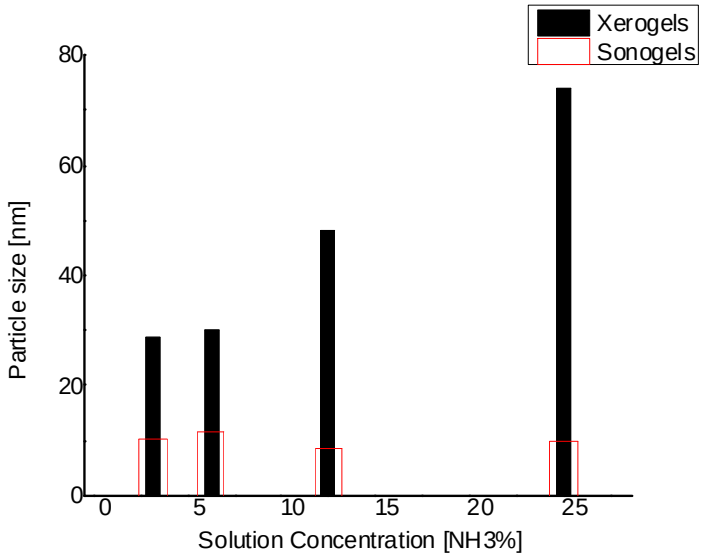
In Figure 7 was exhibit the correlation between the xerogels/sonogels total pore volumes related to supplied NH_3 solution concentration.
From Figure 7 it can be seen that in the case of xerogels series the catalyst dilution was most favourable in order to increase the total pore volume. In the case of sonicated series of samples, the highest total pore volume (0.44cm^3/g) was obtained for 12% NH_3 concentration of catalyst supplied solution. The total pore volume for entire sonicated series presents significant increased values than that of silica xerogels series.

Figure 7 Pore volume related to ammonia solution



Based on N_2 adsorption-desorption isotherms, specifically by using BET technique [7] derived surface area values, the particle size have been calculated with the equation: (D) = $\frac{6}{S_{BET} \cdot d_{SiO_2}}$; where amorphous silica density was, $d_{SiO2} = 2.2$ g/cm^3 [8].
Figure 8 represents the correlation between the particles sizes correlated with the supplying NH_3 solution concentration for both series of samples.

Figure 8 Particle size related to ammonia solution



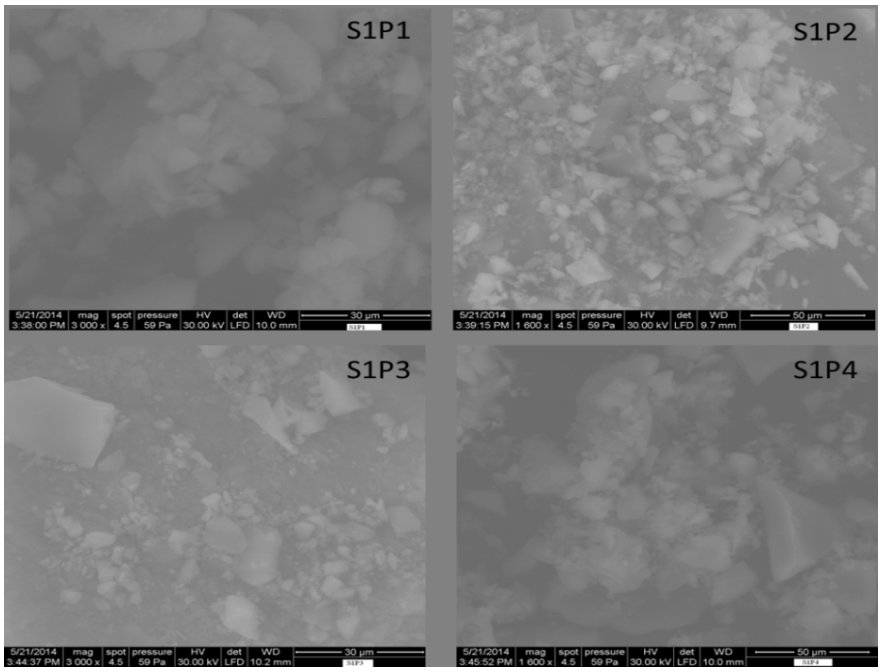
From Figure 8, it can be observed that for xerogels series, particles size significantly decreases with the concentration of supplied NH_3 solution concentration. In the meantime for the sonicated series, particles size has not been significantly influenced by the supplied catalyst solution concentration. A small particles size for sonogels can be observed at critical

concentration of the ammonia (25% NH_3). The particles size decrease with the increasing of ammonia supplying solution concentration. Therefore, for the most concentrated sonogel sample S2P1 (25% NH_3) the particles size was 9.9 nm related to the most diluted sample S2P4 (3% NH_3), where the particles size was 10.5 nm.

SEM

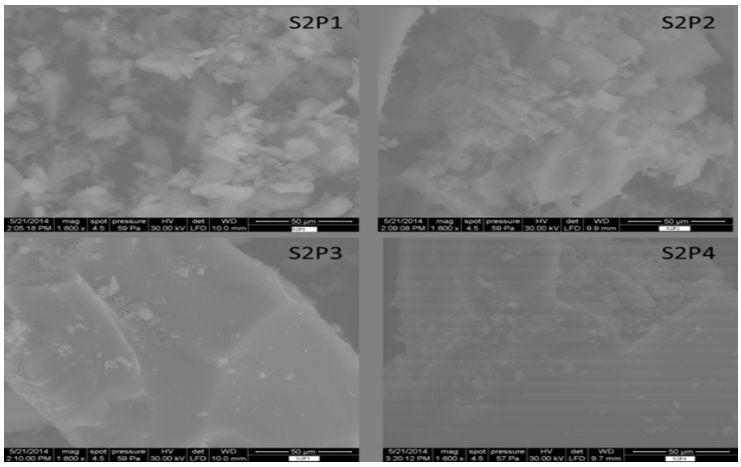
Figure 9 and Figure 10 shows SEM image of silica xerogels prepared from silica sols with mean particles sizes of ~45 nm for xerogels and ~10 nm for sonogels. The prepared silica nano-powders show the irregular agglomerated silica particles. The irregular shape of silica particles could be caused by the fast nucleation process, which is difficult to be controlled in alkaline environment [6].

Figure 9 Xerogels SEM image



For xerogels, it was observed asymmetrical formations heavily agglomerated. In the case of sonicated samples S2P3 (6% NH_3) and S2P4 (3% NH_3) the SEM images showed a bulk structure.

Figure 10 Sonogels SEM image



FT-IR

In the case of both synthesized samples, at room temperature, the infrared spectra exhibit a broad band at 3400 cm^{-1} due to absorption of bridged hydroxyl group. The broad band from 3400 to 3800 cm^{-1} specifically for sonogels, was ascribed to OH stretching vibrations, bridges between adsorbed water and OH of Si-OH groups or stretching of OH from bridged Si-OH groups [12]. The band due to the bending vibration of molecular water (1640 cm^{-1}) was also present in the FTIR spectra and can be used to study the adsorbed water. The absorption bands at 1093-1100 cm^{-1} is attributed to stretching vibration of Si-O bond. The 800 cm^{-1} band corresponding to the ring structure of SiO_4 tetrahedral and the 464 cm^{-1} band correspond to deformation vibration of Si-O-Si [13], [14], [15]. The results of FT-IR spectra were exhibited in Figure 11 and Figure 12.

Figure 11 Silica xerogels FT-IR spectra

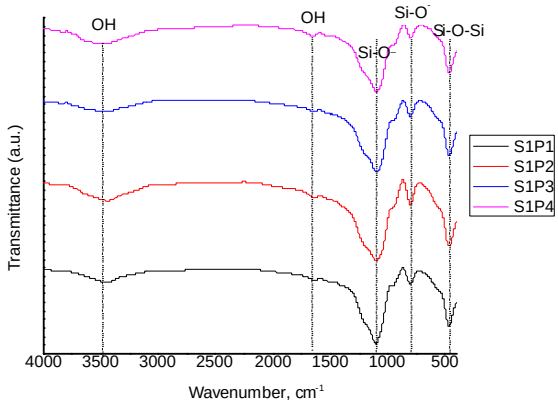
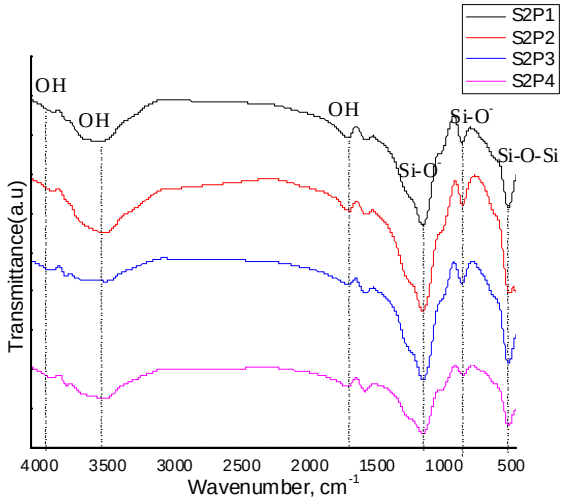


Figure 12 Silica sonogels FT-IR spectra



4. CONCLUSION

The investigation showed that by keeping rigorously constant all reactants molar ratio TEOS: H_2O: ETOH: NH_3 = 1: 25: 20: 0.2 and by supplying different concentrations of NH_3 catalyst, the synthesis outputs changed significantly. The surface area of xerogels was situated up to ~100 m²/g while the sonogels have two-three times higher surface area up to ~300 m^2/g. Base concentration by changing pH had the different effects on particles morphology. In case of xerogels and sonogels with the highest ammonia solution concentration it could be seen a more porous structure, due to the formation of particles (depositing of precipitated particles in solutions). For all concentrations of ammonia solution silica precipitates were obtained, by classic sol-gel process and relatively stable translucent silica colloids, under ultrasonic field action. Pore size distribution for sonogels was significantly narrower (~6-9 nm). The sizes of silica colloids decreases with increasing the ammonia concentrations, the number of nuclei was larger and therefore smaller silica colloids are obtained. In the case of highest ammonia catalyst (25%NH_3), larger particles precipitated, so that the formation of a stable suspension of silica particles was not possible to form because the nucleation process produced primary particles nuclei and therefore larger silica particle size was formed. At high pH values, where the particles may have a high solubility in the sol, more porous structures are obtained, the particle sizes increases. SEM image reveals that the particles start to agglomerate in the alkaline media (NH_3); it was observed that the structure start to modifying leading to irregular silica shapes. From FTIR spectra has been shown that all xerogels/sonogels samples presented silica similar bands corresponding to –OH and –Si-O groups. The SiO_2 particles size was found to increase with ammonia concentration up to 0.01 M (NH_3 25%), for ammonia concentration under 0.01 M, the particles size decrease.

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