Arab J. Nucl. Sci. Appl., Vol. 53, 4, 122-133 (2020)

Arab Journal of Nuclear Sciences and Applications

ISSN 1110-0451 **Web site: ajnsa.journals.ekb.eg** **(ESNSA)**

Gamma - Radiation-induced reaction of Sulfuric Acid with Silica Gel: A Novel Method for the Formation of sulfonic Acid-Functionalized Silica (SiO_2-SO_3H)

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Received 3rd March 2020
Accepted 14th Sept. 2020

The radiation-induced reaction of sulfuric acid with silica gel (SG) was carried out using γ-radiation from a ^{60}*Co* source at room temperature and, its mechanism were suggested. The formation of sulfonated SG (SiO_2-SO_3H) was confirmed by IR, thermal analysis (TGA/ DSC). Elemental analysis and morphological structure of treated SG ($SG_{treated}$) was investigated by scanning electron microscopy (SEM). According to the comparison of the SEM images of SG and $SG_{treated}$, it seems that irradiation of SG in the presence of sulfuric acid leads to partial segmentation of SG particles. The IR spectra of the treated silica ($SG_{treated}$) is different from that of the SG. Where, peaks related to the presence of sulfunic group are observed, as well as shifts of SG peaks due to treatment. Moreover, TGA/ DSC of $SG_{treated}$ is different from that of SG. Elemental analysis reveals that particle size of SG affects the S/O % value, where $SG_{treated}$ with >0.16mm - 0.2mm particle size has the maximum value. Also, S/O% value, of >0.16mm - 0.2mm SG particle size, increased, linearly, with absorbed dose up to 80 kGy and then decresed at higher doses.

Keywords: Silica gel; Sulfuric acid; Gamma radiation; Sulfonic acid - functionalized silica

Introduction

Chemical modification of SG surface has been growing in the recent years [1]. SG have been Chemically modified, i.e. functionalized, via surface hydroxyl groups as anchor points [2-4]. Generally, immobilized reagents on inorganic solid supports show several advantages such as ease of recyclability and purification of the catalyst [5,6]. Many conventional attempts have been conducted for the synthesis of solid sulfonic acid functionalized silica (SiO_2-SO_3H), such as the reaction of chlorosulfonic acid with SG [4,7-13]. In this view, several types of SiO_2-SO_3H have been synthesized and applied in catalyzing chemical transformations and organic synthesis [6,11,13]. The use of SiO_2-SO_3H as a catalyst in organic synthesis has attracted great interest. Therefore, SiO_2-SO_3H catalyst was used for alkylation [14], esterification [15], nitration [16], acetylation [17] formylation [18], heterocyclic synthesis [9,19], and Sulphonation [20]. Moreover, SiO_2-SO_3H was used for heavy metal ions removal from aqueous solutions [21], such as, uranium recovery from granite leach solutions **[**22]. Moreover, modification of surfaces with superhydrophilic/moieties [4] is important in fabrication of electrical conducting materials. Therefore, a new proton-conducting membrane was prepared by the addition of SiO_2-SO_3H [23**]**, where, SiO_2-SO_3H can improve the proton conductivity of the Nafion/SiO2, which can be used in proton exchange membrane fuel cell

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DOI: 10.21608/ajnsa.2020.25092.1333

(PEMFC) [24]. Moreover, the incorporation of SiO_2-SO_3H with high surface area in an organic polymer matrix enhances the water uptake and conductivity properties [25]. Although many studies have been published on classical synthesis of SiO_2-SO_3H , no data on its radiation-induced formation was available. Therefore, the present work aims to study the γ-Radiation-induced formation of silica bonded -sulfonic acid by radiolysis of sulfuric acid in the presence of silica gel.

Experimental

Different particle size samples (≤0.16mm, >0.16mm - 0.2mm, >0.2mm - ≤0.5mm), of SG were obtained by sieving (60-100 meshes-Merk) after washing by double distilled water and drying at 100C°. Sulfuric acid 95-97% from Merk was used without further purification. In 20 ml bottle, 10 ml sulfuric acid was added to 2g of SG (preheated at 100 for 12hours).

Samples were irradiated at ambient temperature using γ-rays from a 60-Co source of NCCRT at dose rates in the range 1.11kGy/h. After irradiation, the SG were filtered, thoroughly washed with *double distilled* water and soaked therein overnight to remove the residual (non - bonded) sulfuric acid, the samples were then dried in oven at 100°C to constant 12 hours.

Infrared Spectroscopy FT-IR

FTIR spectra (from 4000 - 400 cm^{-1}) of the SG before and after radiolytic treatment (irradiation with Sulfuric acid) were obtained at room temperature with a BRUKER Vertex70 spectrometer (Billerica, MA, USA) at a resolution of 2.0 cm^{-1}.

Thermogravimetric analysis (TGA/ DSC)

Thermogravimetric analysis (TGA/ DSC) of the SG samples before and after radiolytic treatment was performed using thermo-gravimetric analyzer instrument (Simultaneous DSC/ TGA- SDT Q600 USA). About 10 mg of powder samples was heated in an alumina holder in air or nitrogen (flow rate 100 mL/min). Analysis was carried out in the temperature range from 20 °C to 1000 °C at a heating rate of 20 °C/min.

Scanning electron microscopy (SEM) and elemental analysis (EDX)

Surface morphological study of the prepared samples was carried out using a Scanning Electron Microscope (SEM) (JEOL-JSM-5400-Japan), operated at an accelerating voltage of 30keV. In addition, qualitative and quantitative elemental analysis of the samples under investigation was performed using an Energy Dispersive X-ray analyzer (EDX) (OXFORD-ISIS-UK) attached to the above-mentioned model of the JEOL scanning electron microscope.

RESULTS AND DISCUSSION

The possibility of SG surface sulfonation via radiolysis of SG in the presence of concentrated sulfuric acid was characterized by studying IR spectra, TGA, DSC thermograms and SEM and EDX elemental analysis.

SEM micrographs of SG and SG $_{(treated)}$

Scanning electron micrographs of SG and SG $_{(treated)}$ samples at magnification x100 are shown in Fig. (1).

From the micrographs (Fig.1A) and (Fig.1B), it can be observed that both images of the particles have different morphological nature, where SG $_{(treated)}$ (Fig.1B) sample has a rougher surface than that of the untreated SG (Fig.1A). This difference may be due to the irradiation of SG in the presence of H_2SO_4. The micrograph of $SG_{(treated)}$ (Fig.1B), reveals the presence of many segments as compared to SG (Fig. 1A). This can be assigned to the rupture of SG particles due to irradiation in the presence of H_2SO_4, where, Si─O bonds can be ruptured by radicals such as H atoms [25a], which can be formed during radiolysis. Reformation of ruptured Si─O can be hindered via the reactions of the free radicals of ruptured Si─O with other irradiation produced radicals.

Effect of SG particle size

EDX was used to determine the elemental percentage of S and O for samples with different SG particle size (ps) irradiated (80 kGy) with concentrated sulfuric acid. Table1 illustrates, beside the S% and O%, the S/O%. It is obvious that the maximum S/O% ratio was observed in the presence of SG ps ”>0.16mm - 0.2mm”. The minimum S/O% ratio was observed in the case of ps ((≤0.16mm) sample, although, ps ”≤0.16mm” corresponds to the highest surface area in this study. This can be attributed to that, the higher the number of silanol groups present on the surface the more hydrophilic the silica surface is. Therefore, in the case of the smallest particle size (≤0.16mm) silica particles, spontaneously, adhere together by the cohesive forces (hydrogen bonding) [26]. As the ps increased (>0.16mm - 0.2mm), adherence of the SG particles decreased, where the cohesive forces and consequently, the mutual particles attraction become lower relative to that of "≤0.16mm" [26]. Consequently, S/O% reaches the maximum value in the presence of ps ">0.16mm - 0.2mm". Further increase in ps (>0.2mm - ≤0.5mm) will lead to slight decrease in S/O%. This behavior can be related to the increase of the overall surface area of the SG particles as their particle size decreases, consequently, the available OH groups, for reaction with H_2SO_4, will decrease [26]. Moreover, the pore diameter is proportional to the particle size and varies inversely with specific surface area. Therefore, the smallest particle size has the highest surface area, and consequently the smallest pore diameter [26]. Consequently, in the case of the smallest pore diameter, the diffusion of the, large, sulfuric acid molecules may be hindered and consequently their reactions with silanol groups present in the pores.

Effect of absorbed radiation dose

It was observed previously that the maximum S/O**%** of irradiated SG/H_2SO_4 system was obtained with ">0.16mm - 0.2mm" ps. Consequently, such particle size (>0.16mm - 0.2mm) was used in the study of the effect of absorbed radiation dose on S/O**%** of SG/H_2SO_4 system. Figure (2) illustrates the increase in the S/O**%** as absorbed dose increased up to79.6 kGy. The S/O**%** decreases with further dose increase.

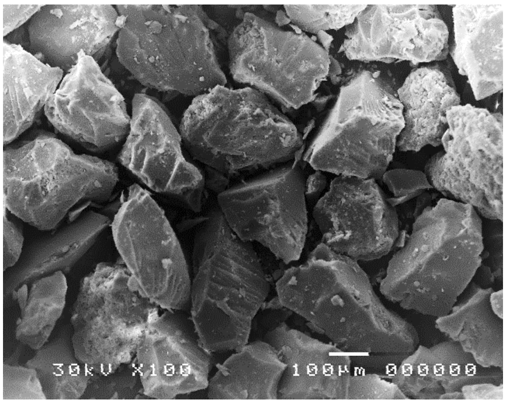
Thermo-gravimetric analysis (TGA)

The thermal behavior of SG and $SG_{(Treated)}$ was studied by thermo-gravimetric/differential thermal analyses (TGA/ DSC). Although, several workers studied TGA/DSC of SG indirect bonded to sulfonic groups [27, 28], no data were published on the thermal analyses of SG directly bonded to sulfonic groups. In the current study, thermal degradation was investigated in the range 30 – 1000 °C under air (oxidative atmosphere) or nitrogen to study/ approve the properties , and formation of sulfonated SG in the current study. The TGA thermograms in air (Fig.3) show two characteristic decomposition stages. It is obvious that that allover the run the residual weight of $SG_{(treated)}$ is higher than that of SG.

In fig.(3), upon comparing the first weight loss (around 100°C) in SG and $SG_{(treated)}$ thermograms, due to physically bonded water on the surface [27,31-33], it is clear that there is a difference in the amount of water loss. Where, the weight loss is higher in the case of SG (16%) , than $SG_{(treated)}$ (14%). Which can be attributed to the super-hydrophilicity of $SG_{(treated)}$ surface due to the attached sulfonic groups [33,34]. Therefore, the holding efficiency (hydrogen bonding strength) of water is higher in the $SG_{(Treated)}$ and, consequently, lose of water will be less than in the case of SG. Moreover, it is observed that the weight loss stage of $SG_{(Treated)}$ is shifted to higher temperature (102°C) relative to that of SG (95°C). This shift indicates that the $SG_{(treated)}$ has a higher hydrophilic property, i.e., water strongly adsorbed. Moreover, in the thermogram of $SG_{(Treated)}$, it was observed that, weight loss region in the temperature range of 200 to 600°C, can be due to the oxidative decomposition of sulfonic acid group [27,29,30,35]. Also, the weight loss in temperature range "200 to 600°C' can be due to water loss caused by the strong hydrogen bonding among water molecules, and the sulfonic acid groups attached to silica gel [27]. It should be mentioned that the 'strongly bound water' around the sulfonic groups (hydrated water) can remain attached with the sulfonic group until its thermal decomposition [36]**.** This process is nearly completed up to about 200–600°C[35,37]. At higher temperature (700-1000 °C), the slow, continuous weight loss was, probably, due to the condensation of vicinal silanol groups leaving siloxane groups [38]. Moreover, it is obvious that the final residue, at 1000 °C, is higher in the case of $SG_{(Treated)}$ relative to that of SG (fig.3) which, can be attributed to the product of entra-estrification reaction between sulfonic groups and vicinal silanol groups.

Figure (4) illustrates differences of DSC thermograms of SG and $SG_{(Treated)}$ in air. The thermogram of $SG_{(Treated)}$ shows three endothermic peaks (1,2,4) and one exothermic peak (3). Endothermic peak (1) is related to the desorption of physically bonded water [31] and confirms the initial weight loss observed in the TGA analysis. Also, peak (2) can be related to strongly bonded water to sulfonic groups [31], as well as, silanol groups. Exothermic peak (3) can be assigned to oxidative decomposition of sulfonic groups. It should be mentioned that peak (3) is slightly shifted to higher temperature relative to corresponding exothermic peak in SG thermogram. Endothermic peak (4) may point to a chemical reaction(s) between remaining sulfonic and silanol groups

Figure (5) reveals the effect of gas atmosphere on the thermal degradation of SG and $SG_{(Treated)}$. It is obvious that weight loss of $SG_{(Treated)}$ is higher than that of SG when the thermal analysis is carried in N_2 gas. Interestingly, this situation is the reverse of that in air (Fig.3), in which weight loss of SG is higher than that of $SG_{(treated)}$. This important observation confirms the reaction of sulfuric acid with SG. Moreover, in air, it seems that O_2 may, either oxidizes, stabilizes, or enhances its reaction of sulfonic groups with other species, such as silanol groups. Where, in nitrogen atmosphere, such reaction may be hindered.



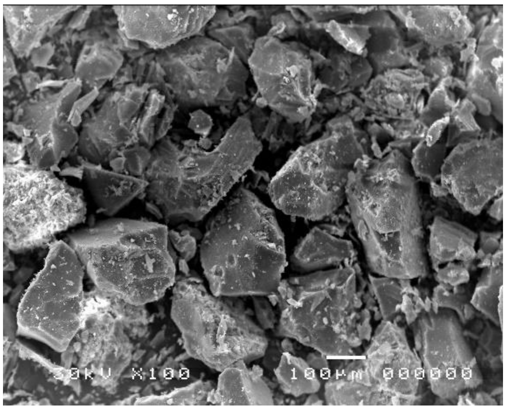


Fig. (1): SEM micrographs of (A) SG (left) and (B) SG $_{(treated)}$ (right)

Table (1): Effect of SG particle size on the S%, O%, and S/O%

ps	S%	O%	S/O%
≤0.16mm	**0.2**	**2.3**	**8.7**
>0.16mm - 0.2mm	**0.4**	**2.0**	**20.0**
>0.2mm - ≤0.5mm	**0.3**	**1.8**	**16.7**

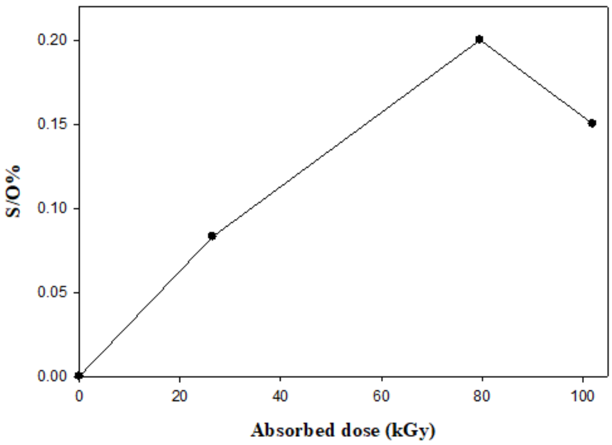


Fig. (2): Effect of absorbed radiation dose on S/O% (according to EDX surface analysis), dose rate = 1.11kGy/h.

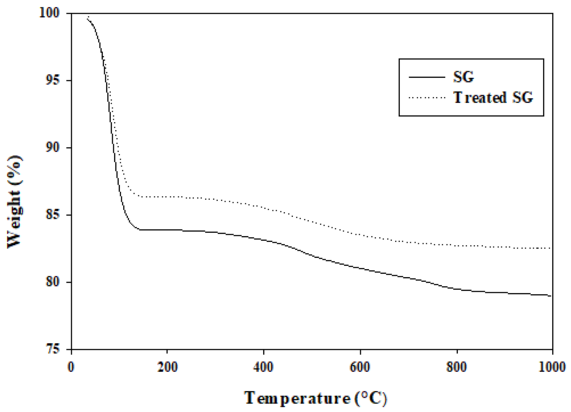


Fig. (3): Thermograms of SG ──, SG $_{treated}$ …… from RT up to 1000°C, in air (20°C/min).

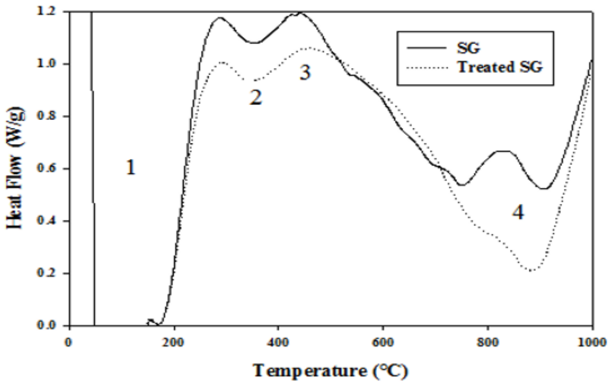


Fig. (4): DSC thermograms of SG and $SG_{(Treated)}$ in air.

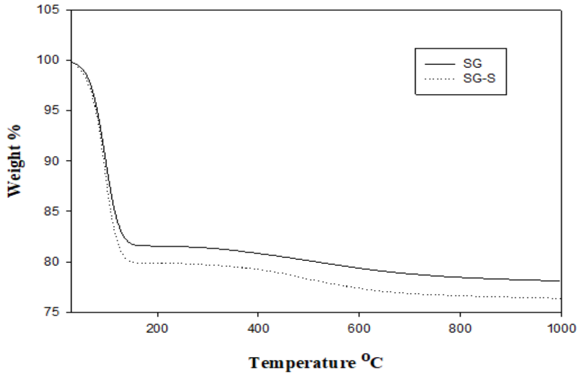


Fig. (5): Thermograms of SG__ and $SG_{(Treated)}$ ……in N_2

Infrared spectroscopic analysis (FT-IR)

The FT-IR spectrums of the SG and $SG_{treated}$ were recorded in the frequency range of 4000–500 cm^{-1} in order to verify the presence of sulfonic groups on the SG surface. Assignments of the main bands are based on literature values [39-41]. Generally, it is observed that there are differences in IR peaks shape (hights) as well as shift in IR peaks location in the IR spectra of SG and $SG_{treated,}$ specially, in finger print region. These shifts of peaks locations indicate a chemical modification of the surface of SG. Moreover, the appearance of some peaks indicates the sulfonation of the SG surface. So, Fig.(6) illustrates partial spectra (450-620 cm^{-1}) of SG (A) and $SG_{treated}$ (B). In these spectra, a slight red shift of peaks at 456.26 (Si-O-Si out of plane bending/ symmetric stretching) [42,43] and 560.25 cm^{-1}(Si-O-Si stretching modes) [43] was observed, while, peak at 606.59 cm^{-1}, due to Si-O bending[44] was blue shifted to 611. 44 cm^{-1}. The red shift of the peak at 456.26 cm^{-1} (Si-O-Si out of plane bending) to 455.43 cm^{-1}, and peak at 560.25 $cm^{-1}$to 557 cm^{-1} in $SG_{treated}$, can be attributed to the presence of sulfonic groups attached to SG. Also, the blue shift (606.59 cm^{-1}→ 611. 44 cm^{-1}) can be related to the bending vibrations of sulfonic acid groups .Where, the SO_2 scissors absorb in the range 520-610 cm-1 [45]. Also, it seems that the peak at 606.59 (SG), due to Si-O- bending [44] is blue shifted to 611. 44 due to sulfonic acid groups substitution –Ve inductive effect (–I)[46]. Moreover, Table 2 and Fig.(6) shows that the peak height ratio (557/455) in spectrum B (0.089) is higher than that of (560/456) in spectrum A(0.058). Also, peak height ratio (606/455) in spectrum A(0.092)is higher than that of (611/455) in spectrum B (0.072) (Fig.6).

Figure (7) illustrates partial spectra (790 – 970 cm^{-1}) of SG (A) and $SG_{(Treated)}$ (B). A slight shift was observed in both peaks observed in this range. The peaks at 798 (in both spectra, A and B) are assigned to Si-O-Si stretching vibration [43]. Moreover, the blue shift in the peak at 963.15 to 964.54 cm^{-1} can be attributed to the –I of the sulfonic gp [46].

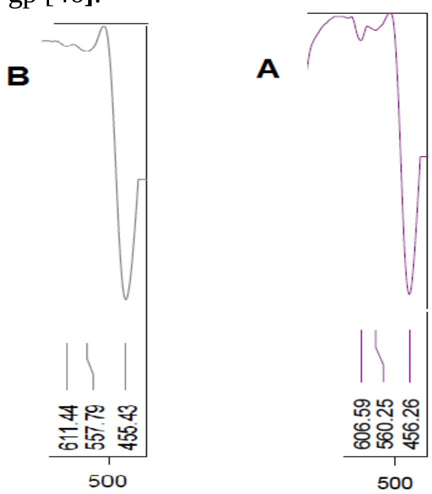


Fig. (6): Partial spectra (450-620 cm^{-1}) of SG (A) and irradiated SG in the presence of H_2SO_4 (B)

Table (2): Peak hight ratio of 560/456 and 606/456 in the spectrum of SG (Fig.6A) and 557/455 and 611/455 in the spectrum of SG $_{(Treated)}$ (Fig.6B)

SG peak ratio (560/456) (fig.6A)	SG (Treated) peak ratio (557/455) (fig.6B)	SG peak ratio (606/455) (fig.6A)	SG (Treated) peak ratio (611/455) (fig.6B)
0.058	0.089	0.092	0.072

It should be mentioned that, SG peak ratio (963/798), in spectrum, Fig.(7A) (1.28), increased in spectrum ,Fig.7B,(1.35) (Table3).

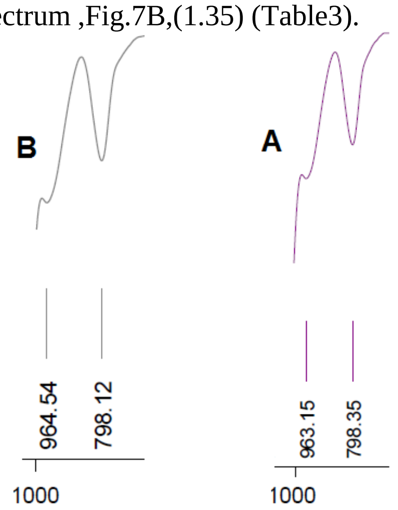


Fig. (7): Partial spectra (790 – 970 cm^{-1}) of SG (A) and $SG_{(Treated)}$ (B)

Table (3): Peak height ratio of 963/798 in the spectrum of SG (Fig. 7A) and 964/798 in the spectrum of $SG_{(Treated)}$ (Fig. 7B)

SG peak ratio (963/798) (Fig.7A)	SG $_{(Treated)}$ peak ratio (964/798) (Fig.7B)
1.28	1.35

However, characteristic peaks of the -SO_3H group are located in 1000-1100 cm^{-1}[47], which coincides with the enhanced appearance of the peak at 1067 cm^{-1},Where the band at 1067. 66 cm^{-1}(Fig.8) can be assignment to S=O symmetric stretching modes of sulfonic acid groups, substituted at SG[48].

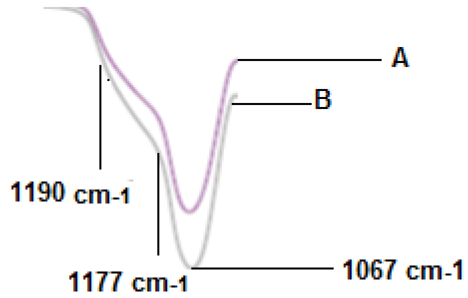


Fig. (8): Partial spectra (900 – 1200 cm^{-1}) of SG (A) and $SG_{treated}$ (B).

Also, the sholder (1170-1190 cm^{-1}) can be attributed to the presence of sulfonic groups (SOH bend) [49**,** 50**]**. Where, a doubly degenerate asymmetric stretch SO_3 between1123 and1302cm^{-1} is observed **[50**].

Figure (9) illustrates the blue shift of peak at1984.91 cm^{-1}, due to association of H_2O [51], in partial spectrum 9A, to 1987. 46 cm^{-1} in partial spectrum 9B. The band at 1987. 46 cm^{-1} can be assigned to the presence of hydroxonium/bisulfate on the SG surface [50]. Figure(10) shows that, both SG (A) and $SG_{(Treated)}$ (B) exhibited a very broad peak at 3200–3600 cm^{-1}, which resulted from the SiO-H vibration [43]. The shift of the broad band from 3262.56cm^{-1} before treatment of SG (due to asymmetric and symmetric O-H stretches) to 325450 cm^{-1} after treatment, can be attributed to the hydrophilicity of sulfonic group attached on the surface of SG [52]. Where, O-H streching vibration will be red shifted via strong hydrogen bonding [53] of the hydroxyl groups with the sulfonic group on the surface of SG. It can be proposed that hydrogen bonding between hydroxyl groups and sulfonic group is stronger than mutual hydrogen bonding of hydroxyl groups.

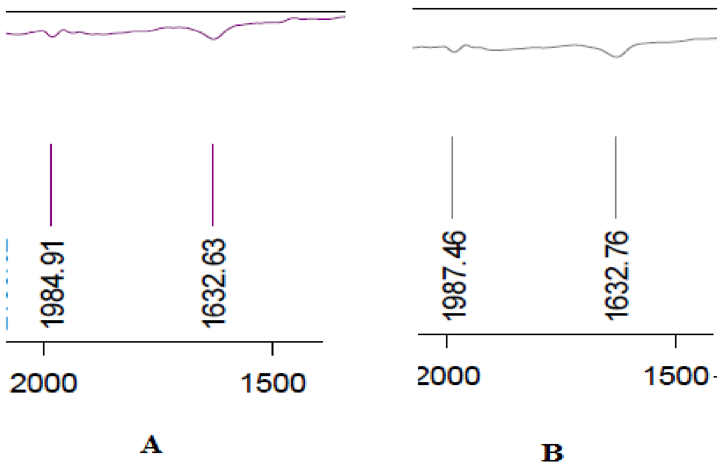


Fig. (9): Partial spectra (2000 – 1500 cm^{-1}) of SG (A) and SG$_{(Treated)}$ (B).

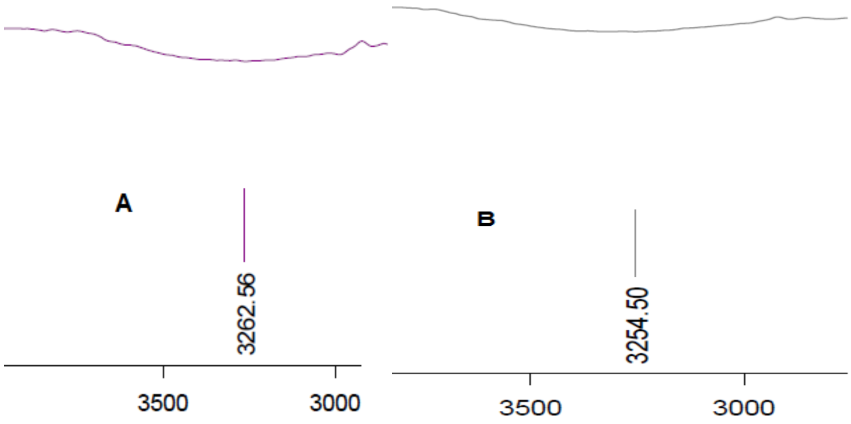


Fig. (10): Partial spectra (3500 - 3000 cm^{-1}) of SG (A) and SG$_{(Treated)}$ (B)

Mechanism of sulfonation of SG surface

Radiolysis of H_2SO_4 was studied by several authors [46,54, 54a,55]. It was proposed that the main radiatiolysis products of H_2SO_4 are H_2O, SO_2, $(S_2O_3)_x$, H_3O^+, HSO_4^-, and SO_4^{2-}[54]. Loeffler et al. [54] proposed that, excited H_2SO_4 ($H_2SO_4^*$) is formed upon radiolysis, which can be followed by ionization:

$$H_2SO_4 \xrightarrow{ww} H_2SO_4^* \quad (1)$$

$$H_2SO_4 \xrightarrow{ww} H_2SO_4^+ + e- \quad (2)$$

Formation of SO_3 can take place via dissociation of excited H_2SO_4 ($H_2SO_4^*$) and $H_2SO_4^+$ recombination with an electron (eqs.3,4):

$$H_2SO_4^* \rightarrow H_2O + SO_3 \quad (3)$$

$$H_2SO_4^+ + e- \rightarrow H_2O + SO_3 \quad (4)$$

Formation of SO_2 was, also, proposed via some reaction with bisulfite (HSO_3) radicals:

$$H_2SO_4^* \rightarrow OH + HSO_3 \quad (5)$$

$$H + HSO_3 \rightarrow H_2O + SO_2 \quad (6)$$

Moreover, Radical disproportionation involving HSO_3 can form SO_2:

$$HSO_3 + HSO_3 \rightarrow H_2SO_4 + SO_2 \quad (7)$$

Such radicals could combines with OH radical forming bisulfite radical:

$$OH + SO_2 \rightarrow HSO_3 \quad (8)$$

On the other hand, radolysis of SG [56] can be illustrated in the following reactions:

$$SG \xrightarrow{ww} SG^* \quad (9)$$

$$SG \xrightarrow{ww} SG^+ (+eV\ hole) + e- \quad (10)$$

Where, SG^* represents excited SG.

Energy deposition in SG appears in the aqueous phase as solvated electrons. On the other hand, holes remain trapped in the silica phase. Oxidation of OH^- by the +ve hole (in the surface of irradiated SG) produce the hydroxyl radical (·OH) [57]:

$$OH^- + {}^{+}ve\ hole(h^+) \rightarrow OH \quad (11)$$

The OH radicals produced from eq (11) can participate in (eq.8), through which HSO_3 radicals are produced. Moreover, exciton (excited electron and a hole in the valence band remain bound together) can participate in the formation of $SiO^·$ [58]:

$$^3exciton + SG\text{-}OH \rightarrow SG\text{-}O^· + H \quad (12)$$

Where, ^{3}exciton; represents triplet state exciton and SG-OH represents silanol group on surface of SG. It was proposed that, this surface effect decreases as the size of the SG particle size increases [58].

It was ,also , suggested that positive holes can react with SG-OH groups to give $SG\text{-}O^·$ [58]:

$$SG\text{-}OH + {}^{+}ve\ hole(h^+) \rightarrow SG\text{-}O^· + H^+ \quad (13)$$

Therefore, sulfonation of SG surface can be carried out via combination of HSO_3 radical (formed from eqs (5,8) with SiO. (formed from eqs12,13) on the SG surface(eq.14):

$$SiO^· + HSO_3 \rightarrow SiO\text{-}HSO_3 \quad (14)$$

Aslo, $SiO\text{-}HSO_3$ can be formed by the reaction of $SG\text{-}O^·$ (from eq.12,13) with SO_3(from eq. 3,4):

$$SiO^· + SO_3 \rightarrow SiO\text{-}SO_3^· \quad (15)$$

$$H + SiO\text{-}SO_3^· \rightarrow SiO\text{-}HSO_3 \quad (16)$$

Finally, it should be mentioned that H atoms, which are formed during radiolysis, such as from eq.12, can induce rupture of Si-O bonds [25a] and, consequently, the appearance of many segments of SG in SEM images (Fig.1).

Conclusion

Silica surface is considered to be covered with a monolayer of silanol groups. Therefore, the expected radiation-induced reaction of sulfuric acid with SG will be happened on the surface only. EDX scanning confirms the presence of sulfur on the surface of $SG_{(Treated)}$. Moreover, images of both SG and $SG_{treated}$ reveal that, irradiation of SG in the presence of H_2SO_4 leads to a partial segmentation of SG particles. Quantitative scanning of the $SG_{(Treated)}$ shows that S% and O% are affected by particle size of $SG_{(Treated)}$. It was found that as particle size decreases from ">0.2mm - ≤0.5mm" to">0.16mm - 0.2mm", S/O% increases. Further decrease in particle size(≤0.16mm) leads to a significant decrease in S/O%. Which is attributed to the spontaneously adherence of SG particles together by cohesive forces. Consequently, the available surface area for reaction with sulfuric acid will decrease. The effect of absorbed radiation dose on S/O% was found to increase linearly as the absorbed dose increases up to 79.6 kGy,in the case of ps >0.16mm - 0.2mm. Further absorbed dose increase, will lead to a significant decrease of S/O%. This observation can be attributed to the destructive effect of γ- radiation on the sulfonated SG.

Comparison of the thermal stability of SG and $SG_{(Treated)}$ reveals that the 1st weight loss (around 100^{o}C, due to physically adsorbed water) is different. So, in the range, rt - 100 ^{o}C (in air) the weight loss of SG (%) is higher than that of $SG_{(Treated)}$ (%). Which can be related to that, water is strongly hold on $SG_{(Treated)}$ relative to SG. Where, sulfonation increases the hydropholicity of the surface. Therefore, the amount of desorbed water may be taken as evidence of the success of the sulfonation of SG. Above 200^{o}C and up to 800 ^{o}C the weight loss can be attributed for the loss of strongly bonded water to sulfonic groups and the oxidative decomposition of sulfonic groups. Obove 800 ^{o}C the slow and continuous weight loss was due to the condensation of vicinal silanol groups leaving siloxane groups. The DSC analyses for $SG_{treated}$ showed endo- and exothermic peaks consistent with the thermal loss behavior in the TGA analyses. DSC thermogram illustrates three endothermic peaks, which related to the two weight loss stages of TGA analyses. So, the 1st strong DSC endothermic peak around 100°C confirms the loss of physiosorbed water. The 2nd weak and broad endothermic peak in the range 250-480 °C can be attributed for the loss of strongly bonded water to sulfonic groups. An exothermic weak and broad peak in the range > 480- <800 °C, can be assigned to the decomposition of sulfonic groups. The 3rd endothermic peak, centered at 900 °C may point to a chemical reaction(s) between remaining sulfonic and silanol groups. It is worth to mention that the final residues, after heating samples up to 1000 °C in air, reveal that the total weight loss in the case of SG is 21%, while that of $SG_{(Treated)}$ is 18%. Interestingly, in N_2 atmosphere, the total weight loss is higher in the case of $SG_{(Treated)}$ (23.65%) relative to that of SG(21.92%), which is contrary to the corresponding results in air atmosphere. Accordingly TGA of both SGand $SG_{(Treated)}$ are affected by the atmosphere gas (air and N_2) which reveal the role of O_2 on the $SG_{(Treated)}$ thermal degradation.

A comparative investigation, on the IR spectra of SG and $SG_{(Treated)}$, reveals a difference in fingerprint region, and blue and red shift all over the spectra. Moreover, a relative variation in the peak heights was also observed upon such comparison. Peaks which indicate the presence of sulfonic group on the SG surface, can be observed in the $SG_{(Treated)}$. It should be mentioned that direct sulfonation of SG by ionizing radiation rout has not been studied before.

Our results seem to be promising, where the procedure of radiation induced formation of "SiO_2-SO_3H" is easier than conventional methods. Further experiment should be carried to improve the radiation chemical yield of "SiO_2-SO_3H".

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