
MODIFICATION OF SILICA GEL SURFACE BY POLYACRYLAMIDE THROUGH THE REDOX INITIATION OF CERIC AMMONIUM NITRATE - SODIUM SULFITE SYSTEM

MAHMOUD M. KAMEL^{*A}, MOHAMED M. ELHAMALI^B, ABUDELRHMAN F. A. MOHAMED^B, AND ASMA S.H.ALI^B

^a *Department of Chemistry, Faculty of Science(Assiut), Al-Azhar University, Egypt.*

^b *Department of Chemistry, Faculty of Science, Sebha University, The Great Socialist People's Libyan Arab Jamahiriya.*

* Corresponding author, Tel.0113033830. E-mail address: mmk.electro@yahoo.com

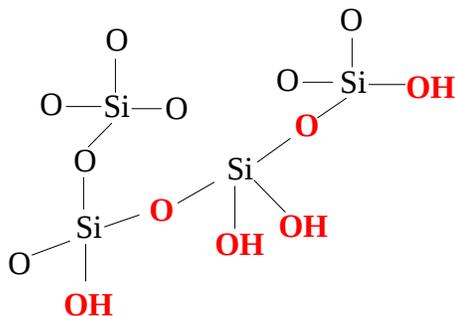
Abstract

In-situ polymerization of acrylamide(AAM) and modification of silica gel surface were extensively studied. The entire different factors affecting the process were optimized aiming at obtaining a product in a maximum yield and high nitrogen content. The obtained results indicated that sodium sulfite is the key issue of the initiation and completeness of both polymerization and modification. Moreover, silica gel itself exerted also an important role in the entire process. The optimum conditions for in-situ modification of 5g silica gel via polymerization of an aqueous acrylamide (5g/50ml) were: 1mM of ceric ammonium nitrate, 120 minutes, 70°C and 0.15g of Na₂SO₃ as an activator. The synthesized modified samples and silica gel were characterized by elemental analysis (only for the modified samples) FT-IR, XRD, SEM, and differential thermal analysis(DTA).

Introduction

It is well known that polymerization of acrylamide proceeds via free radical polymerization which is initiated using different initiators [1-3]. Redox initiators are one of the most efficient types that generate radicals. In such redox reactions, only a small activation energy and lower temperatures are required [4]. This polymerization process taking place in aqueous solution is of interest because the rate constant (k_p) for the propagation reaction is unusually large, the rate constant for termination relatively low and the so called transfer processes (to monomer, to solvent) are very small. As a consequence very long chains (high degrees of polymerization) are created. Besides, polymerization is greatly affected by atmospheric oxygen since it is dramatically inhibited. It can be removed by sparging the acrylamide solution with an inert gas like nitrogen, helium or argon [5]. The use of ceric ammonium nitrate (CAN) has recently received a considerable attention as an inexpensive, nontoxic, commercially available catalyst for various organic transformations to afford the

corresponding products in excellent yields. Due to the numerous advantages associated with this eco-friendly compound, CAN has been explored as an active catalyst for a variety of reactions, oxidation, nitration, 1,3-dipolar cycloaddition, thiocyanation, protection, esterification, 1,4-addition, and the biginelli reaction [6]. Moreover, recent polymerization processes have been involved the redox Ce^{4+}/Ce^{3+} system as an excellent initiator[7,8]. On the other hand, silica gel is the most common adsorbent material and its amorphous form is a polymeric type of silicic acid consisting of a vast network of interconnected micropores. Silica gels have big pore volume with a wide range of diameters – typically between 5Å and 3000Å. Types with an average pore size of about 20Å are known as narrow pores silica gels but silica gels with an average pore size of about 110Å and beyond are called wide pores silica gels[9]. The structure of silica gel[10] is characterized by the presence of a certain functional moieties owing to the presence of some groups such as siloxane, ($\equiv Si-O-Si\equiv$), with the oxygen located on the surface and silanol groups, ($\equiv Si-OH$) [Scheme I].



Scheme I

The surface of silica gel was subjected for several modification studies and a unique review by Mishra et al.[11] has revealed comprehensive methods for the silica gel modification and their applications. Our attempt is based on a modification of the silica gel surface by (PAAM) by in-situ polymerization of the acrylamide monomer using ceric ammonium nitrate as an initiator. A series of experiments were carried out to obtain a product in a maximum yield that having high nitrogen content. So, all factors controlling the process were studied. These factors include initiator concentration, reaction temperature, reaction time and quantity of water as a solvent for the monomer. Since polymerization is greatly influenced by atmospheric

oxygen we are attempting to provide a chemical agent instead of degassing process. It is well known that sodium sulfite is as an oxygen scavenger and good reducing agent [12,13] hence, experiments are particularly examined using different amounts of Na_2SO_3 as an activator of the overall process.

Experimental

Materials

Acrylamide and ceric ammonium nitrate (CAN) of analytical grade reagent were supplied from S.D. Fine Chemical, India. Silica gel was obtained from Northampton, U.K. Nitric acid extra pure was purchased from E.MERCK Darmstadt F.R. GERMANY.

Modification of silica gel

5 g of silica gel was put in Erlenmeyer flask, then an appropriate amount of ceric ammonium nitrate in nitric acid solution (1M) as well as a specific amount of aqueous acrylamide solution and sodium sulfite as a solid were added. The flask was closed and put inside a water bath shaker at a subjected temperature for the desired time under maximum speed stirring. After complete polymerization and hence modification, the reaction mixture was cooled, then an excess amount of ethanol was poured into the obtained product to induce the precipitation. The obtained solid was washed several times with ethanol–water (80:20,v/v) mixture then with distilled water to remove the unreacted monomer and reagents. It was then vacuumed and dried at 40°C to a constant weight. The percentage yield of the modified silica gel was calculated by the following equation:

$$\text{Percentage Yield (\%)} = [(W_m - W_0) / W_0]100$$

Where; W_m and W_0 denote to the weight of the obtained modified silica, and weight of the pure silica gel respectively.

Techniques

Elemental analysis

The elemental analysis of modified silica gel samples was performed using Series II CHNS/O Analyzer 2400, USA.

FT-IR spectroscopy

A Perkin-Elmer 630 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm^{-1} . The IR spectra of silica gel and the modified silica gel were recorded in solid state using a KBr pellet method.

Thermal analysis

The differential thermo gravimetric (DTA) analysis of both silica gel and the modified one were carried out with a PYRIS Diamond TG/DTA Perkin-Elmer, SII Instrument (USA). Sample analyses were performed up to a temperature of 1000 °C, starting from 50 °C in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10°/min.

Scanning electron microscopic (SEM)

SEM studies for both samples silica gel and the modified silica gel were performed using a SEM (JEOL Model JSM-840A, Japan). The samples were coated with gold and mounted on a sample holder. Photographs were taken at an accelerating voltage of 15 kV.

X-ray diffraction

XRD analysis was carried out by A PW 1840 diffractometer and PW 1729 X-ray generator (Phillips, Holland).

Results and discussion

Factors Affecting on the Polymerization Process

Effect of the initiator concentration .1

Firstly, the effect of the initiator concentration on polymerization of acrylamide and hence the percentage of the modified silica yield was investigated. Through the results given in Table1, it is obvious that the best concentration of ceric ammonium nitrate is 1mM which led to a 100% reaction yield. Moreover, polymerization of acrylamide and hence modification of silica can be achieved at the concentration of initiator as small as 0.1mM. Thus, the observed increase in the percentage yield of modified silica gel within the CAN concentration range of 0.1–1 mM may be interpreted on the basis of the fact that the increasing concentration of ceric-ions results in an increase in the redox process giving raise to more initiation. Elemental

analysis of some selected modified samples was performed and shown in Table 2. The estimated analyses show the presence of significant amounts of carbon, hydrogen and nitrogen ensuring the achievement of both acrylamide polymerization and modification of silica surface. Moreover, they are convenient to that previously shown in Table1 concerning to the best concentration of CAN (1mM) which showed a high percentage of nitrogen.

Table 1: Effect of initiator concentration (CAN) on the percentage yield of the modified silica gel obtained by polymerization of (AAM)

Concentration of Initiator [mM]	Percentage yield of the Modified Silica (%)
0.10	19.50
0.25	22.00
0.50	71.00
1.00	100.00
2.00	97.72
5.00	91.00
10.00	85.50
20.00	83.50
30.00	78.00

Table 2: Results of elemental analysis for some selected modified silica gel

Concentration of initiator[mM]	Carbon%	Hydrogen%	Nitrogen%
0.10	23.85	4.72	8.77
0.50	25.17	5.12	9.22
1.00	27.95	5.86	10.28
2.00	26.76	5.39	10.07
10.00	26.37	5.43	9.68
30.00	25.64	5.20	9.65

2. Effects of temperature and water volume as a solvent for (AAM)

The optimum concentration value of initiator was taken to figure out the effects of different water volumes (50, 70, and 100 ml) relative to constant weight of acrylamide (5g) along with heating temperature (40, 60, and 70°C) at all other fixed factors. Results illustrated in Table 3, indicate that the higher obtained yield corresponds to 50 ml of water rather than 70 ml and 100 ml. They also showed that a

very small yield was obtained at 40°C and the highest percentage yield(100%) was obtained at 70°C. Results were confirmed through the obtained data of elemental analysis of some selected samples(Table.4). Since a small yield was obtained at a lower temperature (40°C), it seems to be insufficient activation energy for the entire process. Conversely, the highest yield obtained at 70°C indicates that, the temperature value is adequate for activation of polymerization and hence modification. Furthermore, the percentage yield decreases by increasing water volume as a solvent for acrylamide probably due to monomer dilution. We also believe that increase of water may lead to decrease of the rate constant (k_p) for the propagation reaction and increasing of the rate constant for termination.

Table 3: Effect of heating temperature along with the volume of water as a solvent for (AAM) on the percentage yield of the obtained modified silica gel

Temperature °C	(%) Percentage yield of the modified silica gel		
	volume of water(mL)		
	50.0	70.0	100.0
40.0	4.0	2.4	-
60.0	86.0	35.0	-
70.0	100.0	64.0	37.5

Table 4 Chemical analysis for the modified silica gel samples obtained by different temperatures.

Temperature °C	Carbon%	Hydrogen%	Nitrogen%
40.00	11.58	2.68	4.22
60.00	26.52	5.30	9.43
70.00	27.95	5.86	10.28

3. Effect of the overall time on polymerization of (AAM) and the percentage yield of the modified silica gel

The process was carried out at various time intervals between 1-240 minutes. The crucial effect of time is clearly observed through Figure 1 and Table 5 which depicts the elemental analyses of some samples. It is clear that polymerization of (AAM) and consequently the modification were performed after 1 minute, however the small yield percentage was obtained. Results show also that the obtained percentage yield became a maximum value at time of 120 minutes. In contrast, an increasing time over 120 minutes, the percentage yield apparently decreased. Data

of elemental analysis for some selected modified samples related to the effect of time definitely prove our observation. A rapid and significant increase of percentage yield of modified silica gel through the first minute may be referred to a very fast increase of the redox reaction rate of ceric ammonium nitrate. Furthermore, it may also be due to the increase in the concentration of monomer, as well as initiator, and activator concentrations at beginning the process. Accordingly, there will be a steady generation of free radicals increasing thus the initiation and propagation. As time increases, the redox rate per minute decreases, however the initiations as well as chain propagation are still performing and hence percentage gradually increases. The decrease in % of yield beyond 120 minutes is due to the depletion in monomer and initiator concentration as well as an activator.

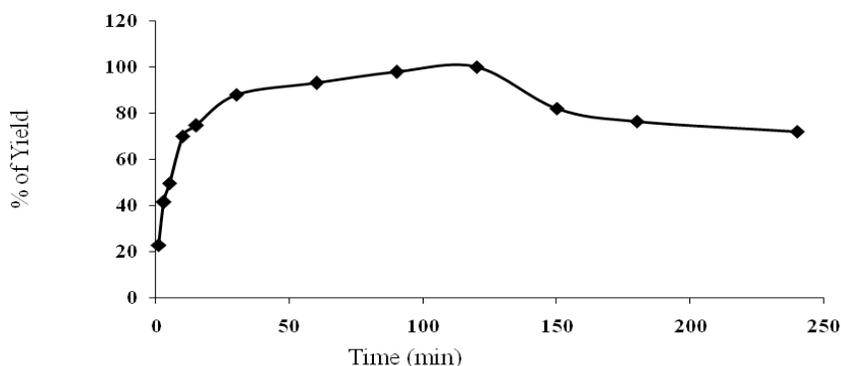


Figure 1: Effect of the overall time on the Percentage yield of the modified silica gel.

Table 5 Elemental analyses for some modified silica gel samples versus the overall time.

Time (minutes)	Carbon%	Hydrogen%	Nitrogen%
1	13.94	3.62	5.28
90	25.86	5.25	9.68
120	27.95	5.86	10.28
240	25.15	5.26	9.14

4. Effect of amount of sodium sulfite used as an activator

Sodium sulfite has an outstanding role in polymerization and modification of silica gel surface. Its influence was studied using 0.01 to 0.2g and fixing the all

previously determined optimum conditions. The results illustrated in Figure 2, show that, at a lower quantity (0.01g), polymerization and hence modification did not take place. By increasing sodium sulfite quantity, the percentage yield gradually increases up to attain a maximum value (106.6%) at 0.15g of Na_2SO_3 . However, exceeding its quantity the apparent value, percentage yield decreased. It is also observed that the mixture became viscous and warm once the quantity of Na_2SO_3 was added indicating the occurring of solution polymerization. The substantial influence of Na_2SO_3 is basically based on its good reducing ability [12]. The reduction of ceric ammonium nitrate leading to a fast free radical formation. Furthermore, it is a good scavenger for oxygen that inhibits polymerization [13]. Hence, the decrease of modified yield beyond 0.15g of Na_2SO_3 may be due to an increase in the rate of ceric ammonium nitrate reduction and there will be a local over concentration of the free radicals which enhance termination process. The obtained result is well evidenced by elemental analyses for some modified silica samples as shown in Table.6.

Ultimately, the optimum conditions for in-situ modification of 5g silica gel via polymerization of an aqueous acrylamide (5g/50ml) are: 1mM of ceric ammonium nitrate, 120 minutes, 70°C and 0.15g of Na_2SO_3 as an activator. The previous optimized factors were applied for running an experiment in absence silica. A surprised result was obtained concerning the yield of product. While the yield in presence of silica was 10.33g, the obtained one in abstracting of silica was 2.6g. In case of silica, the amount of the yield is about 5.33g, after subtracting the initial quantity of silica (5g) this observation certainly suggested that silica gel itself has a considerable effect during polymerization and modification. It may be attributed to the bases that Lewis and acid sites on silica gel [14,15] that can facilitate the formation of monomer radical

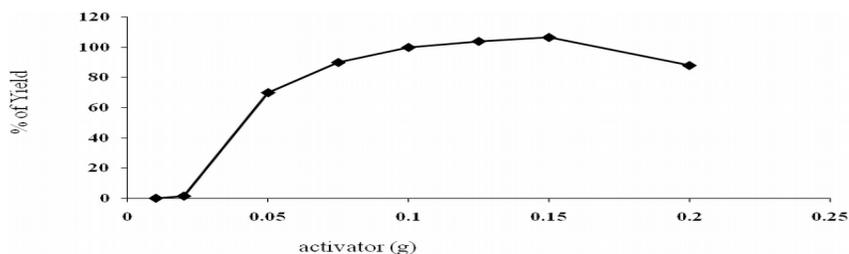


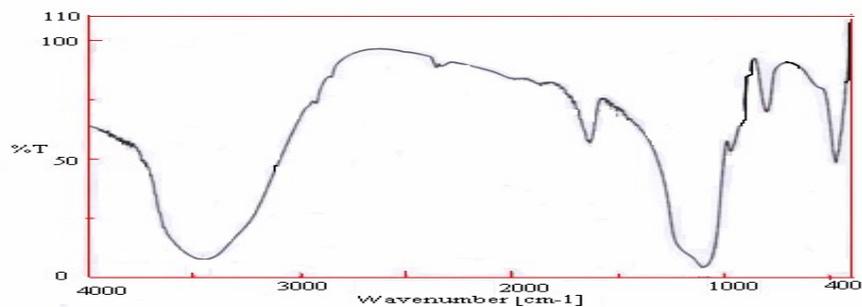
Figure 2: Effect of mass of activator on the percentage yield of the modified silica gel
Table 6 Elemental analysis of some selected modified silica gel samples using various amounts of activating agent(Na₂SO₃)

Quantity of Na ₂ SO ₃ (g)	Carbon%	Hydrogen%	Nitrogen%
0.02	12.87	2.94	4.97
0.05	24.69	5	9.11
0.075	27.27	5.46	9.87
0.1	27.95	5.86	10.28
0.15	35.38	7.15	12.93

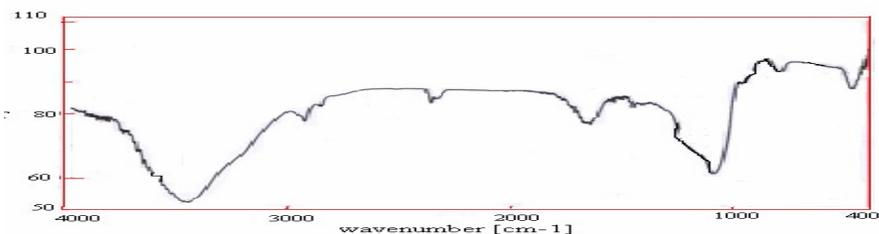
Characterization of the modified silica gel

1. FT-IR analysis

FT-IR spectra of (a) silica gel, and (b) modified silica gel obtained at all optimum conditions are exemplified at Figure 3. The spectrum of pure silica exhibits characteristic absorption bands at 3465 cm⁻¹ (O–H), 1104 cm⁻¹ (asym. ν Si–O–Si), 971 cm⁻¹ (ν Si–OH) and 810 cm⁻¹ (sym. ν Si–O–Si). The broad absorption peak at 3465 cm⁻¹ indicates the hydrogen bonded OH of uncondensed silanol groups (Si–OH). These data are consistent to that published for pure silica [16,17]. Meanwhile, some spectral changes are expected to appear as being associated with the formation of modified silica. The FT-IR spectrum of modified silica gel show bands characteristic of silica as well as a broad absorption peak at 3445 cm⁻¹ is due to the overlap of N–H stretching band of amide group and O–H stretching band. However, the C–N stretching band appears at 1457cm⁻¹. Moreover, the spectrum of the modified silica gel displays two new additional absorption bands corresponding to C=O stretching vibrations of amide at 1653 cm⁻¹, whereas the absorption band at 2926 cm⁻¹ is due to the aliphatic C-H stretching vibrations. Thus, the presence of all new bands in the spectrum of the modified silica certainly implies that the modification process has performed.



(a)

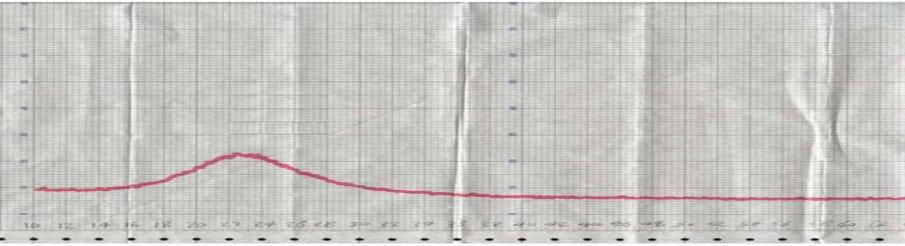


(b)

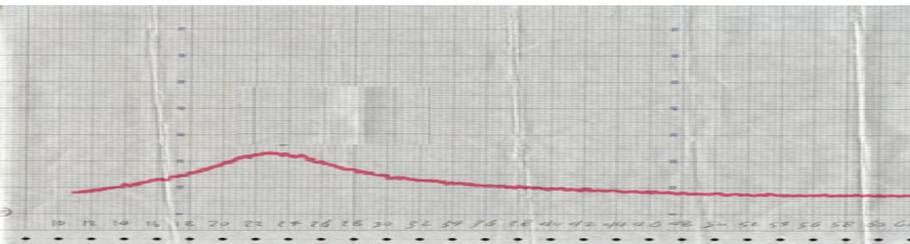
Figure 4: FTIR of silica gel (a) and modified silica gel(b)

2. X-ray diffraction

The X-ray diffractograms of un-modified and modified silica gel samples are shown in Figures 5;a and b, respectively. It is obvious that both silica samples are amorphous while acrylamide is well crystallized [18]. This finding certainly indicates the absence of acrylamide. Moreover, the XRD patterns of silica and the modified one contain strong reflection at $2\theta = 23$. The peak intensity of XRD patterns for two samples are almost the same however, the peak in case of the modified silica, seems to be relatively broad suggesting a possible decrease in its crystallite size.



(a)



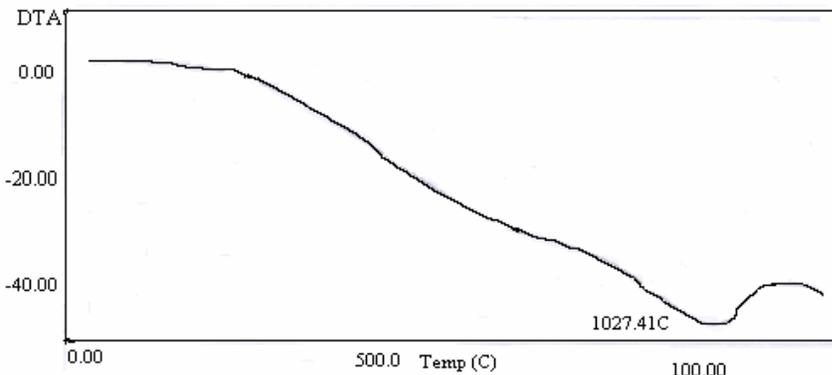
(b)

Figure 5: XRD of silica gel (a) and modified silica gel (b)

3. Thermal

analysis

The DTA curves of un-modified and modified silica gel are shown in Fig 6;a and b, respectively. DTA analysis of silica gel shows a small endothermic peak at 110 °C due to the removal of physisorbed water. The second peak at 1027°C could be the possible phase transformation of SiO₂. Whereas, in the modified silica gel, a small peak at 63.3 may be attributed to loss of the residual solvent used (ethanol), and the peak at 296°C corresponds to the breaking of some carbonyl bonds in the PAAM polymer structure evolving CO, CO₂, and/or ammonia. The second peaks at 626°C which is corresponding to the decomposition of the rigid carbon skeleton polymer. This study also emphasizes the modification of silica by PAAM[18].



(a)

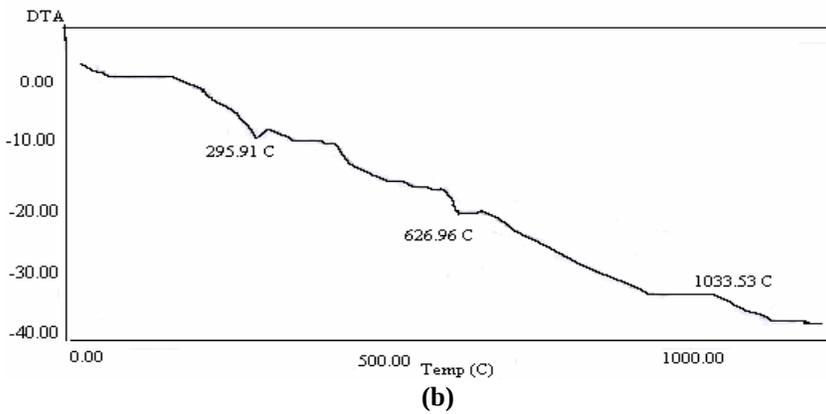


Figure 6: DTA curves of silica gel (a) and modified silica gel (b)

4. Scanning electron microscopy (SEM)

Figure 7 shows SEM for the change in morphological features of (a) silica gel and (b) the modified one with PAAM respectively. The surface morphology of silica gel is totally different from that of the modified one. The SEM image of silica has separate unit cells whereas the surface has been changed and completely covered by fibrillar form after modification. This an important evidence for the formation of silica particles with PAAM domain in the outer shell.

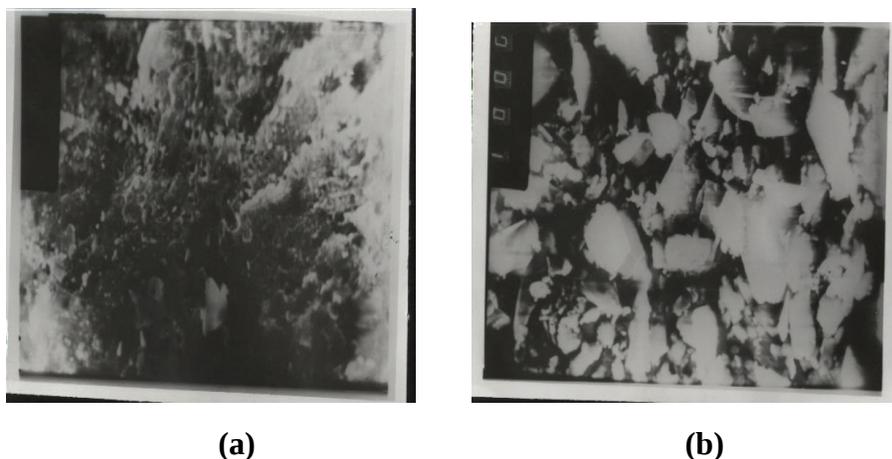


Figure 7: Scanning Electron Micrograph of (a) silica gel and (b) the modified silica gel by PAAM

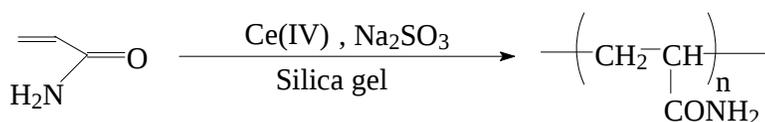
Proposing mechanism of in-Situ polymerization and modification of silica gel with (PAAM)

Through the previously obtained result, indeed the surface of silica gel has been modified by PAAM. Since Na_2SO_3 behaves not only as an O_2 scavenger but also as a good reducing agent for Ce (IV). Meanwhile, Lewis and Brønsted acid sites on silica gel can stimulate the formation of radicals that can be stabilized by the Lewis bases of the silica gel surface. However, in absence of Na_2SO_3 , silica gel did not initiate polymerization reaction, hence its influence was notable in accompanied with Na_2SO_3 . The $\cdot\text{SO}_3^-$ radical has been produced by oxidation sulfite with Ce^{4+} in acid solution [19-21] consequently the polymerization of acrylamide is initiated through the redox reaction involving ceric ammonium nitrate and sodium sulfite. We suggest a possible reaction initially takes place:

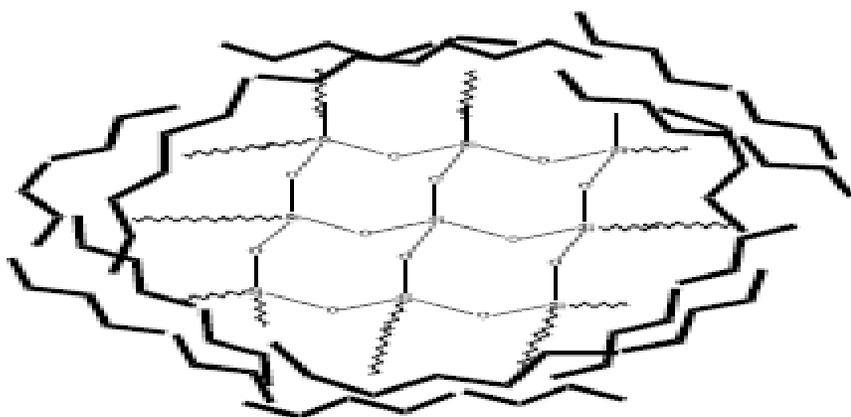


Scheme ii

The $\cdot\text{SO}_3^-$ radical is for the most part a sulfur-centered radical which can act as an oxidant or reductant and like most other radicals may engage in hydrogen abstraction or addition to double bonds such as ($\text{C} = \text{C}$, $\text{C} = \text{N}$, and $\text{C}\equiv\text{C}$) [19-23]. Hence, the initiation presumably takes place through the attack of $\cdot\text{SO}_3^-$ free radical to $\text{C} = \text{C}$ of the monomer vinyl group resulting in an AAM free radical. The obtained radical then attacks the monomer to form a bigger free radical and hence the reaction further propagates to give the polymer. The reaction is terminated either by the combination of two bigger radicals or by abstraction of a proton from the solvent or another monomer molecule Scheme [iii]. The intended mechanism suggests that the initiation and polymerization are involved via vinyl group neither amino group. This observation is apparently demonstrated from the FT-IR spectrum of the modified silica. Since the spectrum does not show the adsorption band of ($\nu_{\text{N-H}} = 3345\text{--}3358\text{ cm}^{-1}$), therefore the backbone structure of the PAAM defiantly exists in the form of $(-\text{CH}_2-\text{CH}-)$. Moreover, appearance all characteristic bands of silica gel. Coated-SiO₂/PAAM hybrid was obtained by physical adsorption of the obtained PAAM on the surface of the silica network. This affords organic-inorganic hybrid composites particles with silica core and PAAM shell and therefore the PAAM shell is expected to dominate the surface characteristics of this type hybrid Figure8.



Scheme iii



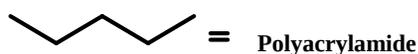


Figure 8: Schematic representation of coated silica gel/ polyacrylamide hybrid material.

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