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SiO_2 PARTICLE EMBEDDED SILICA AEROGELS: ENVIRONMENTAL AND ENERGY APPLICATIONS

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ABSTRACT

The purpose of the study is the preparation of silica aerogels by using the hydro(solvo)thermal synthesis assisted sol-gel method, the preparation of SiO_2 particle-added silica aerogels, and the investigation of their potential use in the environment and energy fields. It has been observed that the prepared silica aerogels can be used removal applications as an adsorbent for 4-nitrophenol, methylene blue, Victoria blue, bromophenol blue organic contaminants. The aerogel was modified nanoparticle as SiO_2 and $-NH_2$ group increasing adsorption capacity minimum 3 fold. The energy application, silica aerogel was used as a catalyst. It has been observed that silica aerogels progressed rapidly in the reaction of $NaBH_4$ with methanol Again silica aerogel was modified increase catalytic activity and prolonging selflife. SiO_2 particles embedded silica aerogel was used same reaction. Self methanolysis reaction was completed about 20 minute at 25 °C. By using protonated silica aerogel, the reaction was completed about 4 minutes at same temperature.

Keywords: Silica aerogels, Hydro(solvo)thermal synthesis, Catalyst, Methanolysis, Adsorption

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1. INTRODUCTION

Silica aerogels are highly porous, open-cell, low-density materials. Since its microstructure consists of nano-sized pores and associated primary particles, it has unique properties such as low thermal conductivity, good sound absorption and refractive index, sound velocity and dielectric constant [1]. Silica aerogels are used in various sectors thanks to their properties.

Silica aerogels are generally synthesized by the sol-gel method. Hydro(solvo)thermal method is considered as synthesis by chemical reactions of substances in a closed and heated aqueous solution or organic solvent at suitable temperature (100-1000 °C) and pressure (1-100 MPa). By using this this method, many compounds or materials with special structures and properties that cannot be prepared from solid state synthesis can be obtained by hydrothermal and solvothermal reactions [2].

The components used during the synthesis of silica aerogel affect the properties of the product. The most frequently used Si precursors are alkoxides such as tetramethoxysilane, tetraethoxysilane (TEOS), polyethoxysilane, methyltriethoxysilane etc. can be used as silica source, as well as water-glass (sodium silicate) solution can be used in the current commercial synthesis of silica aerogels [3].

Mahani et al. used MTMS-based, APD-dried silica aerogels to investigate the effects of sol-gel parameters on the removal of contamination from crude oil in seawater. To investigate the effects of sol-gel parameters, they prepared aerogels under pH values (4 and 8) and various EtOH/MTMS molar ratios, and the adsorption capacity of the prepared aerogels was evaluated for heavy and light

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commercial crude oil under multiple adsorption-desorption cycles. In optimum condition, silica aerogels have reached the conclusion that it can take heavy and light crude oil at 16.7 and 13.7 degrees, respectively [4].

Gu et al. prepared super hydrophobic silica nanoparticles with a short reaction time using a two-step synthesis route using TEOS as a silicon source, NH_4OH as a catalyst and HDTMS as hydrophobic component [5].

Sheng et al. studied the nitrobenzene adsorption of hydrophobic silica aerogels in wastewater and investigated the effects of adsorption density on pH value, adsorption temperature, adsorption time and amount of silica aerogels. They concluded that SiO_2 aerogel adsorption density of nitrobenzene in wastewater can reach 68.76%, the adsorption properties are related to the hydrophobicity of aerogels, the surface area of the organic solution, and the structure of the aerogels [6].

Hrubesh et al. used hydrophobic aerogel in their solvent removal studies and compared their results with standard granular activated carbon adsorption capacities. Using hydrophobic silica aerogel, they compared their adsorption isotherms for % (toluene, ethanol, trichloroethylene, chlorobenzene) in water mixtures with comparable granular activated carbon (GAC) on gram per gram for all solvents tested. The improved performance of the adsorption capacity by aerogel over GAC ranged from factors 30-fold for low molecular weight, highly soluble solvents to 130-fold for non-miscible solvents. They concluded that these significant improvement factors significantly reduced the cost factors that would greatly aid in the use of GAC for VOC capture and solvent cleaning applications [7].

Silica aerogels can be modified with various modification agents to increase their use efficiency. In order to increase the performance of the gels in applications, NH_2 groups have been added with APTES modification then protonated. The addition of new functional groups to the structure increases the application potential of silica aerogel. It allows for new modifications. Sometimes nano/microparticles can be added directly to the medium instead of adding new groups with agents. If the dispersion is well provided, such structures provide an advantage for obtaining tailored materials for specific applications.

In this study, hydro(solvo)thermal assisted synthesis was carried out in a shorter time and in a controlled manner compared to the currently used methods. It was aimed to increase the surface area and increase the application performance by adding SiO_2 particles to the silica aerogels. The application potential of the produced aerogels and their doped forms in the field of environment and energy has been investigated.

2. MATERIALS AND METHOD

2.1. Materials

Tetraethylortosilicate (TEOS, 98%, Sigma-Aldrich), ethanol (99.9%, Merck), ammonium hydroxide (NH_4OH, 26%, Sigma-Aldrich), hydrochloric acid (HCl, 37%, Honeywell), sodium borohydride ($NaBH_4$, 98%, Merck), methanol (99.8%, Sigma-Aldrich), 4-nitro phenol (4-NP, 99%, ABCR), methylene blue (MB, Sigma-Aldrich), bromophenol blue (BFB, AFC), Victorian blue (VB, Acròs). Double distilled water was used throughout the experiment.

2.2. Method

Silica aerogels were prepared in two different combinations which are (1) bare silica aerogels, and (2) SiO_2 nanoparticle embedded silica aerogels. Synthesis stages are shown in Figure1.

2.2.1. Bare silica aerogels, SA

Alcohol/water/TEOS mixture acid-catalyzed hydrolysis and base-catalyzed condensation reactions were carried out at 10-60 minutes time intervals. Afterwards, the mixture was transferred to the autoclave and kept in an oven at 180-200 ºC for 2-72 hours for gelation. The reaction time and temperature parameters were studied systematically to find optimum conditions. Particle doped aerogels were prepared under these specified conditions. The gel was first washed with ethanol and then with an ethanol/water mixture and the impurities were removed by solvent exchange. Afterwards, it was dried by the supercritical carbon dioxide drying method (Figure 1).

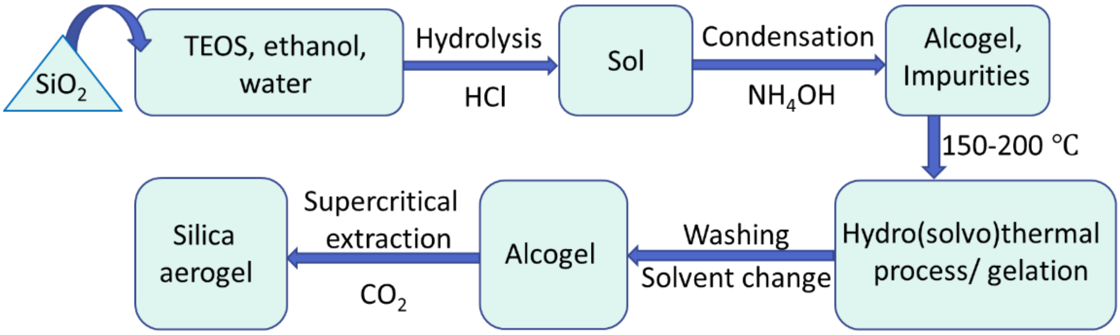

Figure 1. Schematic representation of hydro(solvo)thermal assisted silica aerogel synthesis.

2.2.2. SiO_2 nanoparticle embedded silica aerogels, SiO_2-SA

SiO_2 nanoparticles were added into the silica aerogel and then the above mentioned processes were applied exactly. The SiO_2 nanoparticles were synthesized as monodisperse in different sizes by the Stöber method [8, 9]. The sonicator was used to prevent the nanoparticles added to the medium from collapsing and clumping. SiO_2 particles have -OH groups and their nano-size will play a role in catalytic applications due to their high surface area. It can be modified outside as well as allowing new groups to be added by post modification after the template is placed. Sometimes the particles is used to produce pore/hole by reaction of HF or NaOH.

2.2.3. APTES modification

In order to increase the performance of the gels in applications, amino groups were added with APTES modification and then APTES modified form was protonated. The reaction schematic is shown in Figure 2.

For the APTES modification, 0.5 g of empty aerogel/SiO_2 embedded silica aerogel was taken and mixed with 50 mL of ethanol at 600 rpm for 18 hours. 2.5 mL of APTES and 2.5 mL of water were mixed by vortexing and then added dropwise to the mixture at regular intervals. Stirring was continued for 18 hours. Afterwards, the aerogels washed three times with ethanol, water (1/1, v/v). Then the gels were dried by using freeze dryer.

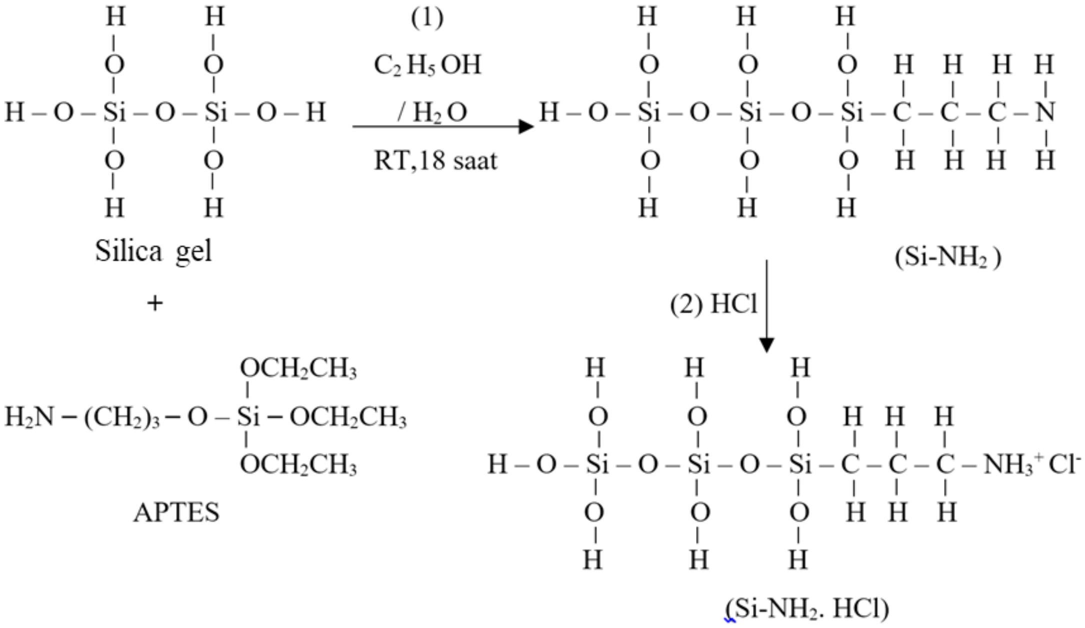

Figure 2. APTES modification to silica gel.

2.2.4. Application studies

In order to increase the performance of the gels in applications, new groups have been added with the modification. The application potential of the prepared silica aerogels in environmental applications as an adsorbent for organic pollutants such as 4-nitrophenol and some textile dyes investigated. To environmental study, removal of contaminant from aqueous media is important. Adsorbent properties important to use real applications. Properties such as high adsorption capacity, easy desorption, reusability, regenerable, having long self-life, handable, easily take after application, being cheap and easily available are some important desired properties. Silica aerogel is stable and different additive could be adding before gelation by dispersing homogeneously. The additive may be chose to increase performance and designed focusing the application. Organic contaminant removal study, knowing adsorbent's surface charge is important to understand interaction of contaminant. When it is necessary to change the charge of the adsorbent, we want to add new functional group to gain opposite charge with contaminant. Another way is directly use polymeric, metallic, or composite particles embedding in the adsorbent.

By using the prepared silica aerogels directly as a catalyst in the reaction of $NaBH_4$ with methanol, its application potential in the field of energy was also investigated. The methanolysis reaction is known acid catalysis, and increased acidity is resulted in high catalytic activity. Silica aerogel was modified APTES adding active $–NH_2$ group to the structure by reacting with hydroxyl group on the silica aerogel. The $–NH_2$ group can be protonated with increasing acidity.

3. RESULT AND DISCUSSION

3.1. Synthesis and Characterization

3.1.1. Bare silica aerogel synthesis and characterization

In order to determine the optimum conditions for silica aerogel production, the effects of factors such as component amounts, pH, mixing time, holding time and temperature on the gelation process were investigated. As a result of the studies, there were cases where polymerization was not observed as well as in particulate and gel structures. In the studies, TEOS was used as the source of silanation, HCl and NH_4OH were used as acid and base catalyst. The optimum condition was reached with a temperature of 180 °C and a holding time of 18 hours, but formation of the gel was observed within 4 hours in the autoclave. The gels after hydro(solvo)thermal synthesis were washed ethanol. Digital camera images of the wet and dried form of the bare silica aerogel and SEM image are shown in Figure 3. As shown the figure, bare wet gel is transparent (Figure 3a). One piece of wet gel was taken and dried by supercritical carbon dioxide drying. After drying so light, transparent silica aerogel was obtained as shown Figure 3(b). Surface morphology of the prepared aerogels was evaluated by SEM. The SEM images of the aerogel can be seen in Figure 3(c) with the porous nature.

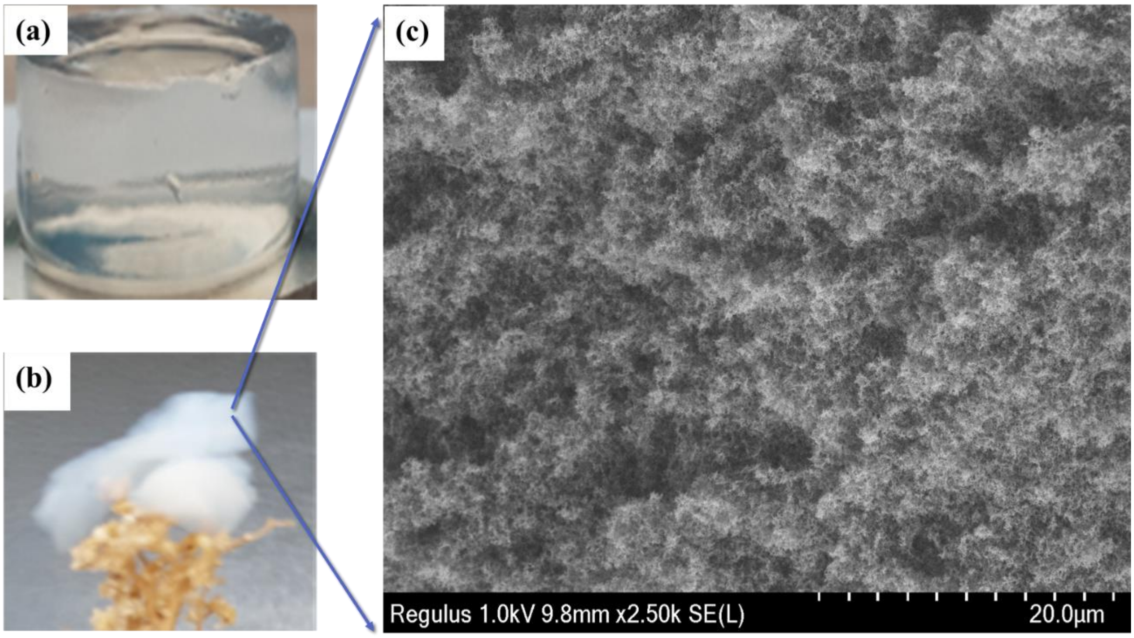

Figure 3. Bare silica aerogel (a) wet state of silica gel digital camera image (b) aerogel dried by supercritical drying, (c) SEM image of bare silica aerogel.

3.1.2. SiO_2 particle embedded silica aerogel synthesis and characterization

To prepare SiO_2 particle embedded silica aerogel, first of all, SiO_2 particles were synthesized by using Stöber method. SEM and DLS methods were used in the characterization of these particles. Results are shown in Figure 4. As shown SEM image, the particles have spherical shape and uniform size. This result supported by DLS measurement resulting 183 nm radius and 0.11 polydispersity index value. SiO_2 particles were synthesized successfully Stöber method. The particle was used to prepare SiO_2 embedded silica aerogel preparation by using same way for the bare silica aerogel.

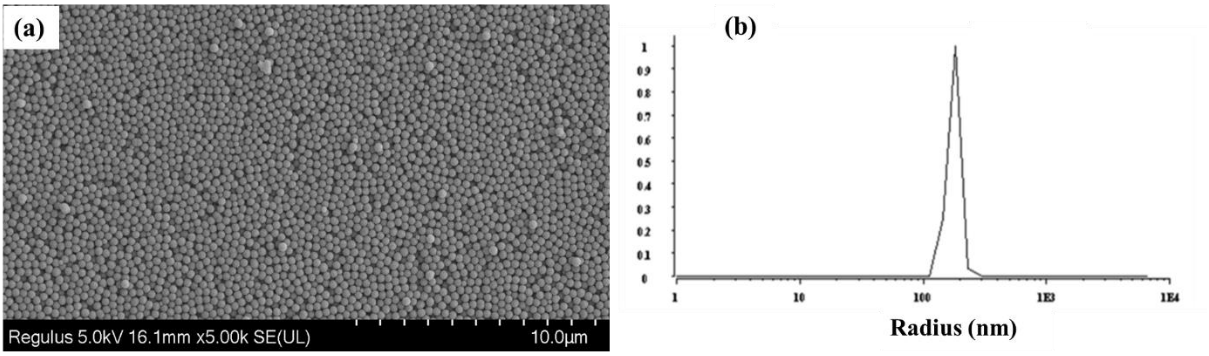

Figure 4. SEM image and DLS result of SiO_2 particle synthesized by Stöber method.

Digital camera images of the wet and dried form of the SiO_2 particles containing silica aerogel and SEM image are shown in Figure 5. As shown Figure 5, SiO_2-silica aerogel' wet form is white. A piece of wet gel was taken and dried by supercritical carbon dioxide drying. After drying so light, whiter than bare one silica aerogel was obtained as shown Figure 5(b). To evaluate surface morphology of the prepared aerogels and to see SiO_2 particles in it was used SEM analyze. The SEM images of the aerogel can be seen in Figure 5(c) with the porous nature and SiO_2 particles.

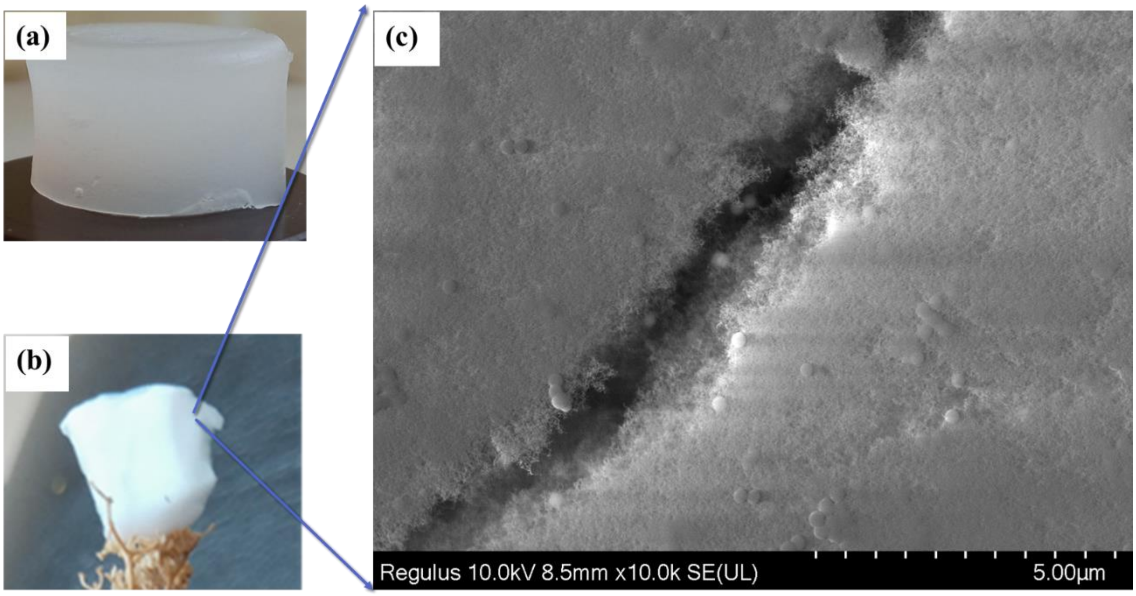

Figure 5. SiO_2 embedded silica aerogel (a) wet state of silica gel digital camera image (b) aerogel dried by supercritical drying, (c) SEM image of SiO_2 embedded silica aerogel.

3.2. Environmental and Energy Applications

3.2.1. Environmental applications

As an environmental application, the aerogels used as a adsorbent for the adsorption/removal of organic contaminant as 4-nitrophenol and textile dyes as methylene blue, bromophenol blue, victorian blue in water has been studied. As shown Table 1, the synthesized aerogels have different adsorption capacity. The aerogel can be modified by adding different functional groups to enhance adsorption capacity.

Table 1. Organic contaminant and dye adsorption on silica aerogels.

Adsorban	4-Nitrophenol (mg/g)	Methylene blue, (mg/g)	Victoria blue, (mg/g)	Bromophenol blue, (mg/g)
SA	41.05	14.09	91.66	5,93
SiO_2-SA	51.76	6.70	84.09	3.39
SA-APTES	137.34	60.14	137.82	10.34
SiO_2-SA-APTES	140.89	44.09	138.26	17.10

The results given in Table 1 obviously say that after APTES modification, the aerogels adsorption capacity increased from 41.05 mg/g to 140.89 mg/g for 4-nitrophenol, from 14.09 mg/g to 44.09 mg/g for methylene blue, 91.66 mg/g to 138.26 mg/g for victoria blue, 5.93 mg/g to 17.10 mg/g for bromophenol blue.

3.2.2. Energy application

For the energy application, silica aerogels directly used as catalyst in the reaction of $NaBH_4$ with methanol to produce H_2. The methanolysis reaction with 50 mM $NaBH_4$ at 25 °C, 1000 rpm without using a catalyst was named as a reference.

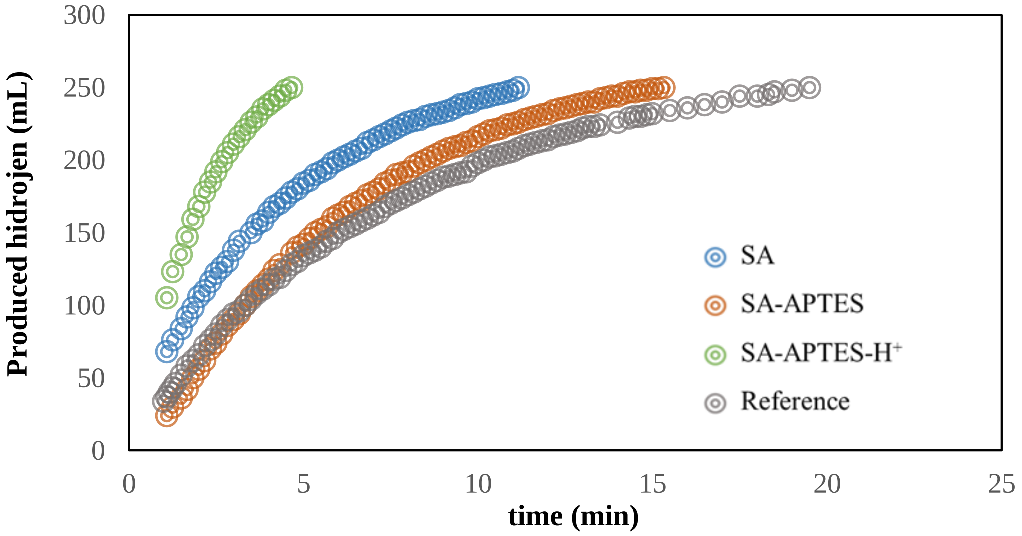

Figure 6. The use of bare silica aerogel and modified forms as a catalyst in the production of H_2 from the reaction of $NaBH_4$ with methanol [50 mg catalyst, 50 mM $NaBH_4$, 25 °C 1000 rpm].

The products obtained by modification and protonation of the synthesized empty silica aerogel with APTES were compared with the reference. It was observed that they played an active role in increasing the reaction rate compared with self methanolysis. The catalytic activities of synthesized silica aerogels were tested using the same catalyst amounts in the methanolysis reaction. When the reaction rates were compared, it was shown that modified and protonated form of bare silica aerogel had higher catalytic activity as in Figure 6.

Reference reaction was performed absence of catalyst and hydrogen production rate calculated as 24 ml/min at 25 ºC. Using SA as catalyst, hydrogen production rate calculated as 39 ml/min at same temperature. APTES modified SA produced 32 ml/min hydrogen, and protonated SA-APTES performed maximum hydrogen production rate as 83 ml/min.

Same result observed for the SiO_2 particles embedded silica aerogel and its modified forms catalytic activity (Figure 7). Using SiO_2-SA as catalyst, hydrogen production rate calculated as 40 ml/min at same temperature. APTES modified SiO_2-SA produced 36 ml/min hydrogen, and protonated SiO_2-SA-APTES performed maximum hydrogen production rate as 50 ml/min.

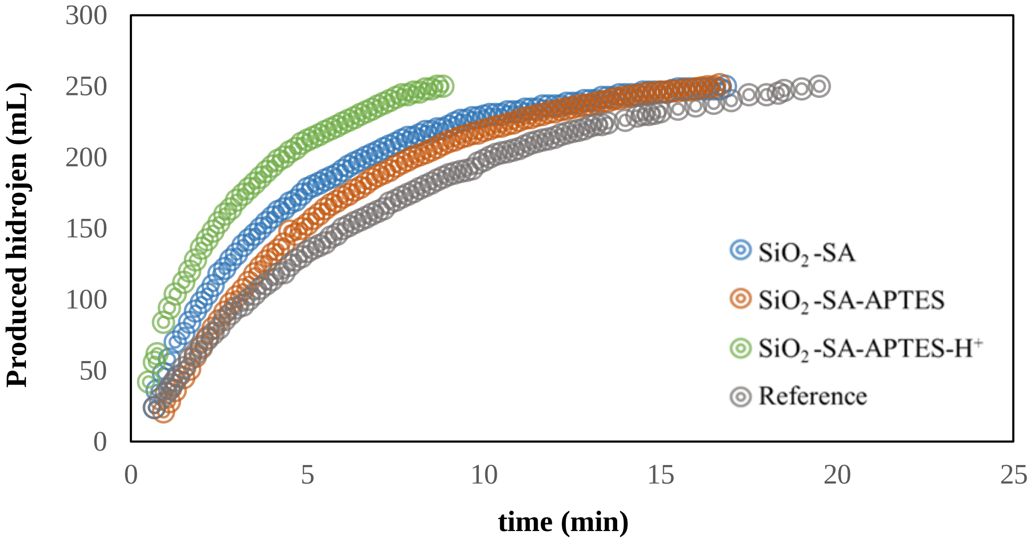

Figure 7. The use of APTES-modified forms of SiO_2-silica aerogel as a catalyst in the production of H_2 from the reaction of $NaBH_4$ with methanol [50 mg catalyst, 50 mM $NaBH_4$, 25 °C, 1000 rpm].

Protonated form of SiO_2 embedded silica aerogel has higher catalytic activity as in Figure 7. The reaction of $NaBH_4$ with methanol is acid catalyzed as supported literature [10-12].

4. CONCLUSION

As a result of the optimization studies, combination ratio of the mixture, pH of the mixture, hydrolysis and condensation time, thermal reaction time, reaction temperature, drying process and time were determined. It has been observed that prepared silica aerogels can be used as an adsorbent for organic contaminant with the increasing capacity 3-fold. An increase in the adsorption capacity of the silica aerogels was observed after modification with APTES. It has been observed that silica aerogels progressed rapidly in the reaction of $NaBH_4$ with methanol as using catalyst silica aerogel and its modified forms. Hydrogen production rate increased from 24 ml/min to 50 ml/min and 83 ml/min by usin protonated SiO_2-SA-APTES and SA-APTES, respectively. These prepared silica gels are promising materials for the environmental and energy applications.

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

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