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Effect of Heat Treatment Temperature and Time on Preparation of Porous Walled Hollow Glass Microspheres (PWHGMs)

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Abstract : The development of hollow glass microspheres (HGMs) with porous walls provides a unique system in which filling agents can be incorporated into the porous walled hollow glass microspheres (PWHGMs). Applications of these have been increased due to the many proposed uses for such a material. They are widely used in various fields of science and technology because of their unique properties, such as catalyst supports, photo catalysts, sorbents, gas sensors, molecular sieves, drug and bioactive delivery systems as well as chemical and biological indicators, etc. PWHGMs with their interior hollow volume and porous walls offer greater storage capacity and pathways for retaining and releasing of stored material. PWHGMs as additives can be used to increase porosity in the electrodes for more electrolyte storage in lead acid batteries and enhance the energy performance of the battery. Further, PWHGMs have potential applications in sensor materials, fuel cells, solar cell, chromatograph column fillers and as micro reactors to encapsulate Pd for catalytic hydrodechlorination of chlorophenols in water. In this research, efforts have been made to prepare PWHGMs from readily available borosilicate glass frits in the laboratory using flame spheroidisation method. The effect of heat treatment temperature and time on preparation of porous walled hollow glass microspheres was investigated. Hollow glass microspheres with wall thickness of 0.5–2 μm were fabricated from borosilicate glass frits in air-acetylene flame. The prepared microspheres were heat-treated and acid leached to produce porous walled hollow glass microspheres. According to results, suggest that heat treatment times used in this research are not as effective as the heat treatment temperatures in changing the porosity (or phase separation) in HGMs and the resulting PWHGMs.

Keywords: Hollow glass microspheres; flame spheroidisation; Borosilicate glass; Porous walled hollow glass microsphere; Acid leaching.

1. Introduction

Hollow glass microspheres (HGMs) are said to be a promising hydrogen storage material and has many advantages over other storage techniques. Due to the unique combination of the spherical shape, controllable size, low density, relatively high strength in uniform compression etc., the HGMs are potential hydrogen storage material. [1]. The main features of HGMs lies in its light weight, low density, nontoxic nature, good mechanical strength, zero environmental pollution, low cost raw material for production of HGMs, the non-explosive nature of the filled hydrogen; ease to handle at atmospheric pressure-temperature conditions and possibility to store in any tank or column. Conceptually, the development of HGMs with porous walls provides a unique system in which various media or filling agents can be incorporated into the porous walled hollow glass microspheres (PWHGMs). Applications of these have been increased due to the many proposed uses of such material. They are widely used in various fields of science and technology because of their unique properties, such as catalyst supports, photo catalysts, sorbents, gas sensors, molecular sieves, drug and bioactive delivery systems as well as chemical and biological indicators, etc. [2] With interior hollow volume and porous walls the PWHGMs offer greater storage capacity and pathways for retaining and releasing of stored material. PWHGMs can also be used as additives wherein it can be used to increase porosity in the electrodes for more electrolyte storage in lead acid batteries and enhance the energy performance of the battery. Further, PWHGMs have potential applications in sensor materials, fuel cells, solar cell, and chromatograph column fillers and as micro reactors to encapsulate Pd for catalytic hydrodechlorination of chlorophenols in water. [3] The structural properties of the HGMs are determined by the initial glass composition, the conditions of heat treatment (temperature, time) and the leaching condition. [4] The main objective of this study is to prepare porous walled hollow glass microspheres with acceptable

quality and investigate the effect of heat treatment (temperature & time) and acid leaching on porosity characteristic of HGMs wall.

2. Materials and Methods

2.1 Preparation of HGMs using Flame spraying method

Hollow glass microspheres (HGMs) were prepared by using of the flame spheroidisation method as shown in the Fig. 1. In this method broken borosilicate glass bottles from the laboratory were crushed to particle size ~1 mm. About 1 kg of the crushed amber glass were further pulverized and sieved to different particle size to get the feed glass powder.

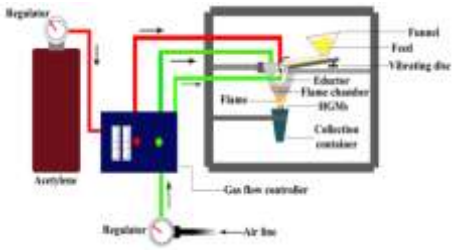

Fig. 1. Schematic diagram of experimental setup for Preparation of HGMs

2.2 Preparation of Porous walled hollow glass microspheres

The Heat treatment of HGMs particles was conducted at different temperatures ranging from 500-600^{o}C and for different time intervals ranging from 8 – 24 hrs. Heat-Treated HGMs were further leached using 3N Hydrogen Chloride. The HGMs were put into the acid for various time intervals. After the process of acid leaching, the HGMs were washed for the removal of the acid. The HGMs, which were floating on the surface, were collected before washing with water, leaving only the sinking particles in the vessel. The formation of PWHGMs was confirmed as the particles that were at the bottom sunk due to the development of pores within the wall as the pores were filled with liquid, forcing the PWHGMs to sink. In order to remove any reaction layer formed during the acid leaching process, the PWHGMs were put into the dilute sodium hydroxide solution. The samples were filtered, washed with sanitized water, and were further sent for characterization analyses. Some of the samples were acid leached without the process of heat treatment to analyze the significance of heat treatment temperature.[5]

2.3. Characterization Techniques

The feed glass powder, the HGMs and the PWHGMs were characterized by using Field Emission–Scanning Electron Microscope (FE-SEM), Fourier Transform Infrared spectroscopy, Optical Microscopy and Environmental scanning electron microscopy (ESEM). FE–SEM JEOL make JSM-7600F was used to study the surface morphology of the feed glass powder, HGMs and PWHGMs. Environmental scanning electron microscopy (ESEM), FEI QUANTA 200 in back scattered electron (BSE) mode was used to examine the shape and size of the pores on the HGMs walls. The spheres were placed as a thin layer on the conductive tape fixed over the sample holder. The holder was loaded into the sample chamber and evacuated. The FTIR spectrum of the feed, HGMs and PWHGMs were recorded in the range 400–4000 cm^{-1}at room temperature on a Bruker Fourier Transform Infrared Spectroscopy (Vertex 80). [6]

3. Results and Discussion

3.1 Experimental Observations

The production of PWHGMs by the process of acid leaching can be confirmed by a simple test.The Fig. 2. (a)shows the image of HGMs in water whereas Fig. 2. (b)shows the HGMs after acid leaching. After the process of acid leaching, the top and the bottom layer as shown in the Fig. 2. (b)are separated.The HGMs particles due to it's light weight and low density floats on the water as shown in Fig. 2. (a).Whereas, the particles that are at the bottom sink due to the chances of development of pores within the wall, forcing the PWHGMs to sink due to its higher density.

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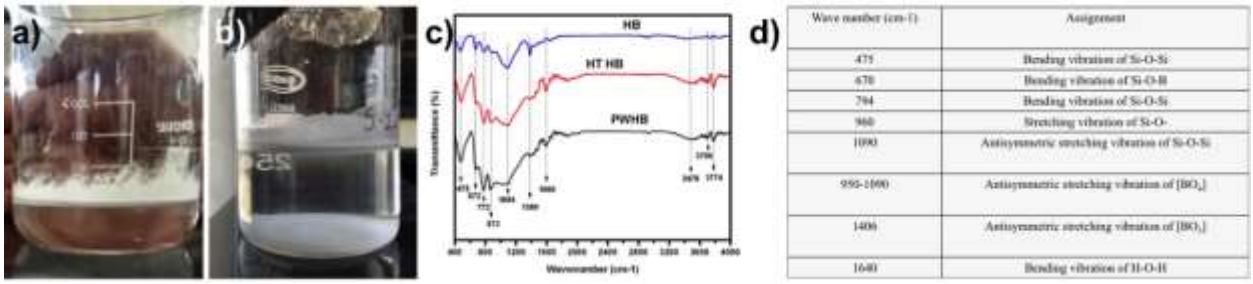
3.2. FTIR studies of the samples

FTIR studies on the product HGMs (HB), heat-treated HGMs (HT HB) and the PWHGMs were conducted and shown in Fig. 2. The FTIR peak assignments and its wave numbers are presented in Fig. 2. (d). From the Fig.2., it was clearly observed that the samples showed IR transmission bands corresponding to the bending, stretching and the anti-symmetric stretching vibrations of the BO4 & BO3bonds. An IR signal observed was at wave number 672 cm^{-1}, corresponding to the bending vibration of Si-O-B. It was seen that the peak of the IR signal at 672 cm^{-1}vanishes as the silica rich phase is increasing. Another IR signal observed was at wave number 1094 cm^{-1} corresponding to the Antisymmetric stretching vibration of SiO_2. It was seen that the peak was broadening as a result of reduction of boron phase and increase of silica phase in the overall composition of the porous walled hollow glass microspheres. A significant IR signal observed was at the wave number, 1380 cm^{-1}, which is corresponding to the anti-symmetric stretching of BO_3 bond. It was seen that the peak of the IR signal at 1380 cm^{-1}vanishes with the formation of pores in the HGMs. Thus from the FTIR analysis of the samples, it can be confirmed that the pores are formed in the HGMs as a result of removal of the boron rich phase after the process of acid leaching.



Wave number (cm-1)	Assignment
475	Bending vibration of Si-O-Si
670	Bending vibration of Si-O-B
794	Bending vibration of Si-O-Si
960	Stretching vibration of Si-O-
1090	Antisymmetric stretching vibration of Si-O-Si
950-1000	Antisymmetric stretching vibration of $[BO_4]$
1400	Antisymmetric stretching vibration of $[BO_3]$
1640	Bending vibration of H-O-H

Fig. 2. (a) HGMs in water (b) HGMs in acid (c) FTIR Studies (d) Peak Assignments

3.3. Surface Morphology Analysis

FEG–SEM images of borosilicate glass and product HGMs are shown in Fig. 3. (a) & (b). The feed particle size in the range 38–63µmwas found to give ~80% conversion to uniform sized HGMs. Hollow glass microspheres with wall thickness of 0.5–2 µm were fabricated from borosilicate glass frits in air-acetylene flame. Fig.3.(c) shows the optical microscopy image of the HGMs, which signifies the presence of cavity in the HGMs produced.

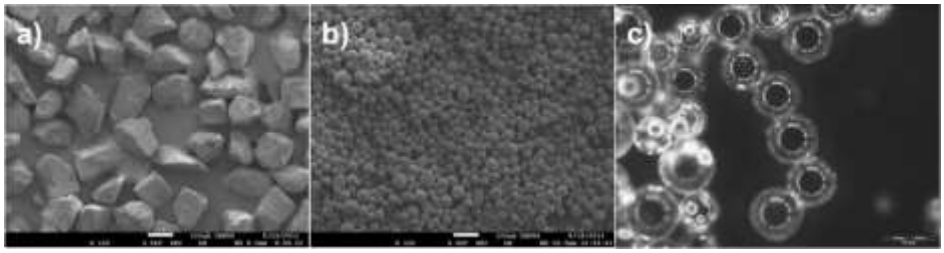


Fig. 3. FEG-SEM images of (a) Borosilicate Feed Glass (b) Product HGMs (HB) and Optical Microscopy image of (c) HGMs

The HGMs were heat treated at different temperatures ranging from 500 – 620°C and at different time intervals ranging from 8-24h. Fig. 4 (a) & (b) shows the SEM image of the heat-treated HGMs at 550°C. The temperature range was taken according to the literature, which was around 500-600°C. HGMs heat-treated at higher temperatures were avoided as at the temperatures above 580°C HGM agglomerates (bonding among the individual HGMs) were formed which can't be separated without applying additional breakage. The Fig. 4 (c) & (d)shows the ESEM images of HGMs heat-treated at higher temperatures.

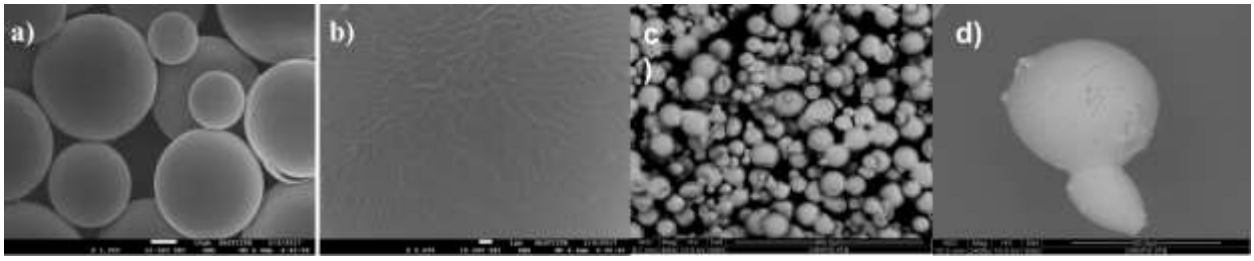


Fig. 4.SEM images of (a) Heat Treated HGMs at 550ºC (b) Magnified image of the surface &ESEM Images of (c) HGMs Heat Treated at high Temperature (d) Magnified image of the surface

The Fig. 5 shows the comparison between the original Feed glass, Acid leaching of HGMs with and without heat treatment. It was observed from the Fig. 5(b) that there was no pore formation on the surface of HGMs. It is due to the lack of phase separation, which occurs at the heat treatment. From Fig. 5(c) & (d) it can be observed that there were some changes in the morphology of the HGMs after acid leaching. Small pores were formed as a result of reduction of boron rich phase.

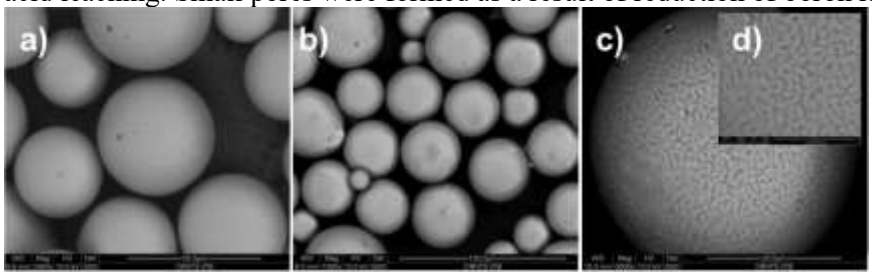


Fig. 5.(a) HGMs Feed (b) Acid Leaching without heat treatment (c) Acid leaching with heat treatment (d) Magnified image of Acid leached HGMs with heat treatment.

4. Conclusion

The Hollow Glass Microspheres of alkali borosilicate glass were fabricated successfully and the formation of Porous Walled Hollow Glass Microspheres was successfully done. Heat Treatment at various temperatures was conducted ranging from 500-620ºC from which 550 °C was chosen to be optimal. The Heat Treatment at higher temperatures resulted in agglomeration. The effect of Heat Treatment Time was found to be not as effective as the effect of Heat Treatment Temperature as there was minimal variation in the microstructure of the HGMs.

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