PREPARATION, CHARACTERIZATION AND PHYSICOCHEMICAL PROPERTIES OF SILICA AEROGEL PRODUCED FROM RICE HUSK

Supported by tetfund TERTIARY EDUCATION TRUST FUND

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Received: June 20, 2017 **Accepted:** September 28, 2017

Abstract: There is an increasing need to preserve the environment in recent times from the global warming perspective. Rice husk when burnt as fuel generates energy and the end product, rice husk ash, which not utilized would result to environmental congestion and pollution; hence the need to find ways to utilize this waste for economic benefits. Silica aerogel was prepared from rice husk ash by sol-gel process. Silica was extracted from the ash as a sodium silicate by boiling it in sodium hydroxide solution. Sodium silicate was neutralized with nitric acid to form silicagel. To prepare aerogel, the pore water of the gel was exchanged with ethanol and then surface modification was done by aging alcogel in ethanol solution. Before drying, ethanol solvent was exchanged with n-heptane. The prepared aerogel was light, crake free solid with bulk density of $0.58g/cm^3$, porosity of 71.0% and refractive index of 1.122. XRD analysis of the RHA fired at 900^0C revealed crystalline structure with particle size of 30.34 nm. The nature of surface modification of the aerogel was studied by Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: Physicochemical properties, porosity, silica aerogel, silica, sol-gel

Introduction

The accumulation of agricultural residue such as rice husk in the environment leads to congestion and pollution. Getting rid of agricultural waste products is a great challenge to waste managers (Godwin *et al.*, 2012; Jemima *et al.*, 2012). A popular and traditional method of decongesting the environment of agricultural waste, especially in Africa and Nigeria in particular, is by burning which cause air pollution by releasing smoke and other harmful gases and particle into the atmosphere. This reduces the air quality and constitutes part of ozone depletion leading to greenhouse effect (Ei-Fadel&Massound, 2001). In a consistent effort to mitigate environmental pollution and congestion by waste disposal, scientists for over the years have been dedicated to researching into better ways of disposing biomass wastes, converting industrial pollutants into harmless forms for disposal, and recycling other waste substances into useful forms that fetch economic benefits. Several waste products generated by man's daily activities can be transformed into other forms that render them economically viable. It is with this drive that scientists have harnessed a way of reducing rice husk through controlled steps to arrive at silica aerogel which find several industrial applications.

Rice hush (RH) is an important agricultural residue (Selvakumal*et al.*, 2014; Rao*et al.*, 2014) rich in silicon which can account for 20% of the 649.7 million tons of rice produced annually worldwide (Ghassan&Hilmi, 2010). It is an economically viable raw material for the production of silicates and silica materials (Yafei*et al.*, 2014). According to Ajay *et al.* (2012) RH is usually high in ash compared to other biomass fuels in the range 10 -20%.

Aerogel is a synthetic porous ultra-light material derived from a gel, in which the liquid component of the gel has been replaced with a gas (IUPAC, 2007). It is a mesoporous (Noor *et al.*, 2013), open cell, low-density substance that exhibits many desirable properties suitable for many industrial applications (Qi & Tao, 2015; Fricke &Tillotson, 1997). Aerogel is used as adsorbent, catalyst support, nanovessels, insulators, sensor material, impedance adjustment, pigment carrier, filters for films, liquids and others (Carlson *et al.*, 1980; Kraume*et al.*, 2002; Vinayak *et al.*, 2011; Nappi, 2010). Silica aerogel were first produced in 1931 by Stephens Kistler by formulation the idea of replacing the liquid phase by a gas with only a slight shrinkage of the gel. Through perseverance and systematic modified approaches, Kistler arrived at aerogel which are very similar to silica aerogels prepared today (Stephens, 1932).

Aerogel are usually prepared by supercritical drying of wet silica gels (Tang & Wang, 2005). The ambient pressure drying technique is one of the alternative cost-effective processes of aerogel synthesis (Rakesh *et al.*, 2009). Other mehods of preparing nanosilica includes the vapour-phase reaction, sol-gel and thermal decomposition technique (Azadeh *et al.*, 2012). The sol-gel process is another method for preparing aerogel using organic silica monomers such as tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS) as precursors. However, report by Kumar *et al.* (2013) holds that such organic precursors are so expensive and carcinogenic hence the need to produce industrial scale silica aerogel from RH, an inorganic raw material which is inexpensive, biocompatible and nontoxic.

Materials and Methods

Materials

The following materials were used in the course of this research work: electric furnace, electric oven, scanning electron microscope (SEM) model Oxford Instrument, X-ray diffractometerXRD6000, fourier transform infrared spectrophotometer FTIR-8400S, routine laboratory wares (PYREX), deionize water, stainless steel beakers, rice husk from Nasarawa town of Nasarawa State of Nigeria. Sodium hydroxide (NaOH), nitric acid (HNO_3), ethanol and n-heptane; All chemicals were of analytically pure.

Methods

Sample collection

Rice husk (RH) used for this research was collected from Beguwa Stone Free Rice Mill in Nasarawa Local Government Area, Nasarawa State, Nigeria at the point of milling. The sample was placed in a clean polythene bag and transferred to the Chemical Engineering Laboratory Complex, Federal Polytechnic Nasarawa.

Sample pre-treatments

Exactly 137.0 g of the Rice Husk was properly washed using deionize water and left to dry in a thermostat oven at a temperature of 110ºC for 24 h.

Ashing of sample

The dried sample was burnt in an electric furnace at a temperature of 900°C for 6 h for complete combustion to occur so that all volatile materials would be removed to obtain the desired ash. Mass of rice husk ash obtained was 26.23 g from the 137.0 g rice husk burnt, while percentage of the ash was 19.15%

Preparation of silica aerogel

About 15 g of ash was mixed with 20 $cm^3$of 30% $^w/_w$ NaOH aqueous solution. The mixture was heated up to its boiling point for 90 min with the reflux. The solution was filtered to remove undissolved residues. The filtrate was neutralized with dilute $HNO_3$to pH of 7 to form silica hydrogel. The prepared gel was aged at room temperature for 24 h under sealed condition. The aged gel was washed using deionized water to remove excess sodium nitrate (Nayak&Bera, 2009).

Subsequently, the silica gel was soaked in solution of 20% ethanol for 24 h, maintained at 50°C followed by aging with ethanol at the same condition. The ethanol treated gel was aged in solution of 70% of ethanol for 24 h at 70°C. According to Nayak&Bera (2009) the strength and stiffness of gel may be increased by ethanol washing due to dissolution of silica from the particles and precipitation into the necks between the particles. Precipitation of silica gives an increase in the density of the wet gel and corresponding strengthening and stiffening of the gel network (Einarsrud&Nilson, 1998). Stated by Nayak&Bera (2009) residual pore water and by-product of condensation is responsible for hydrolysis of ethanol which also takes part in condensation reaction with Si –OH group of gel structure according to the polymerization scheme;

Hydrolysis

$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$ (1)

Condensation

$Si(OH)_4 + (OH)_4Si \rightarrow (OH)_3Si–O–Si(OH)_3 + H_2O$ (2)

$\equiv Si(OC_2H_5) + HO–Si\equiv \rightarrow \equiv Si–O–Si\equiv + C_2H_5–OH$ (3)

The gel was washed with n-heptane several times to remove ethanol solution from the gel. Then, it was aged inside n-heptane at 50°C for 24 h with four times renewal of fresh n-heptane.

Finally, modified gel was aged for another 24 h inside n-heptane at room temperature before air drying. The gel was dried in 24 h interval at 50, 90, 120, and 150°C with partially covered condition and a dried silica aerogel was obtained. A summary of the aerogel preparation steps is as presented in Fig. 1.

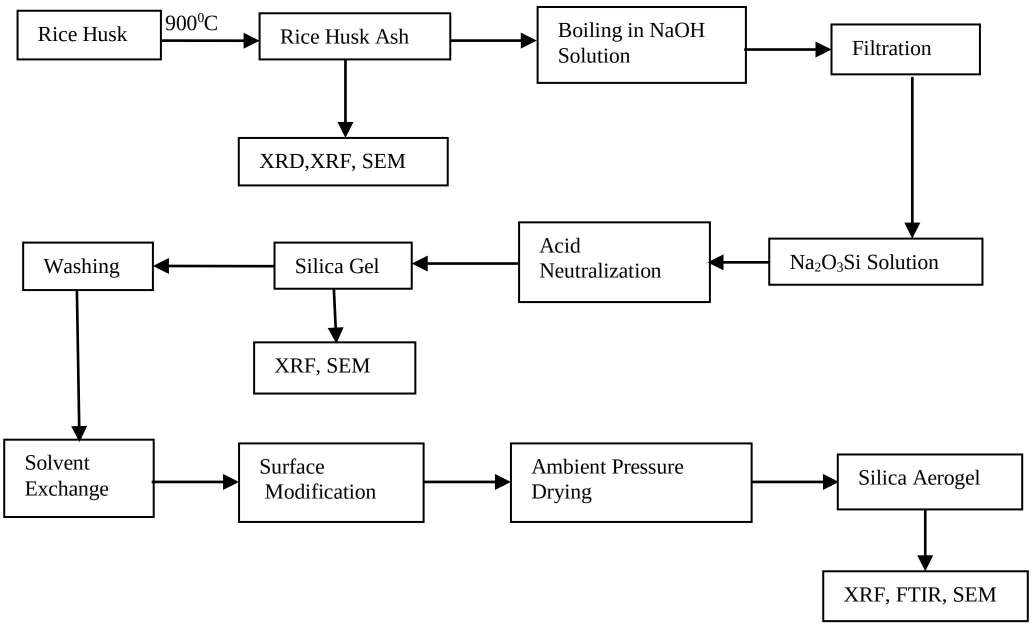

Fig. 1: Flowchart of silica aerogel preparation from rice husk

The bulk density of the sample was estimated using equation A.

$$P = \frac{M}{V} \quad \text{(A)}$$

Where: ρ is the bulk density, M and V are the mass and volume of silica aerogel respectfully.

The porosity of the aerogel was estimated using equation B.

$$P = \left(1 - \frac{\rho_{Si}}{\rho_s}\right) \times 100 \quad \text{(B)}$$

Where: P is the porosity, ρ_{Si} is bulk density of silica aerogel and ρ_S is the specific density of amorphous silica assumed to be 2.0 g/cm^3(Mupa*et al.*, 2015; Adams *et al.*, 2011).

The particle size of the nanosilica was calculated using Debye-Scherrer formula;

$$d = \frac{0.9\lambda}{\beta cos\theta} \quad \text{(C)}$$

where: λ is wavelength of X-ray (0.1541 nm), β is FWHM in radian, θ is the diffraction angle and d is particle size.

The refractive index from the aerogel been density dependent was calculated from the formula

$$n = 1 + k\rho \quad \text{(D)}$$

Where: n is the refractive index, k = 2.1×10^{-4} a constant and ρ (kg/m^3) is the density of the aerogel (Aegerter*et al.*, 2011; Makoto *et al.*, 2012).

Plate 1: Rice husk

Plate 2: Rice husk

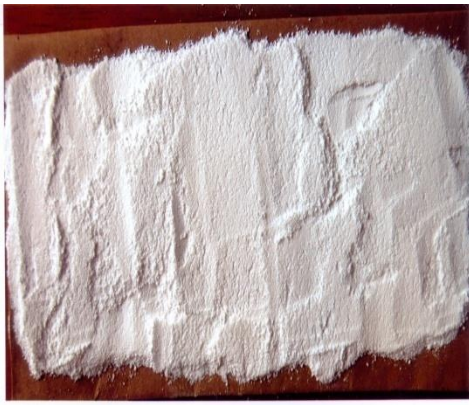

Plate 3: Silica gel

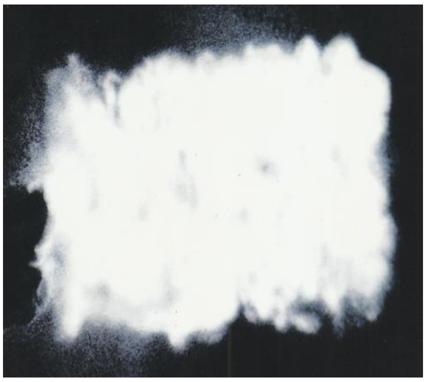

Plate 4: Silica aerogel

Results and Discussion

Chemical Composition of Silica Aerogel

The main aim of converting husk to ash is to utilize its silica for the production of silica aerogel whose percentage varies from one sample to another depending on the climatic and geographical conditions. According to (NIzami, 2003), pyroprocessing of rice husk is frequently carried out to get rice husk ash with maximum percentage of silica with proper processing giving rise to RHA with highest percentage of silica.

High silica content and low levels of elemental impurities are necessary pre-requisite for the synthesis of high purity silicon from RHA (Kingsley, 2010). The chemical composition XRF analysis of the as-prepared RHA revealed 98.32 Wt % $SiO_2$with other oxides totaling to 1.68 Wt %. This result is in agreement with that obtained by Mohamed *et al.* (2015) to be 89.00 Wt% SiO_2.

A comparative study of the elemental composition of silica gel and aerogel is shown on Table 1. Result shows that the concentration by weight percent (Wt %) of silicon 16.7 in silica gel increased to 17.1 in silica aerogel. This is probably due to removal of impurities after soaking in ethanol and treating with n-heptane to remove ethanol solution from the gel which probably hinders a complete detection of the actual composition of silicon in the gel (Pinghua*et al.*, 2016; Kaviyarasu *et al.*, 2016).

Table 1: Chemical composition of rice husk ash heated at 900°C

Element	SiO_2	Na_2O	Al_2O_3	MgO	P_2O_5	SO_3	K_2O	CaO	T_1O_2	Mn_3O_4	Fe_2O_3	ZnO	SrO	Y_2O_3	ZrO_2	BaO
Conc. (Wt %)	98.32	0.04	0.25	0.29	0.32	0.18	0.37	0.35	0.03	0.06	0.39	0.01	0.01	0.02	0.02	0.01

Table 2: Elemental comparison between silica gel and aerogel

Element	Atomic Number	Conc. (Wt %) Silica gel	Conc. (Wt %) Aerogel
N	7	7.1	7.6
O	8	65.1	63.1
Na	11	8.4	5.5
Si	14	16.7	17.1
Rb	37	2.4	6.7

XRD characterization

Phase identification in the RHA was assessed by X-ray diffraction analysis as presented in Fig.2. Generally, silica undergoes structural transformation at different calcinations temperatures (Omotala&Onoja, 2009). Silica obtained at incineration temperatures below 800^0C are amorphous (Ramizanianpou*et al.*, 2009) with broad peaks. Crystalline silica begins to form from 800^0C and is completed at 900^0C (Sugita, 2008). The RHA fired at 900^0C shows significant crystallinity with sharp narrow peaks at 2θ values of 22^0 assigned to MnO and 27^0 attributed to SiO_2. Findings are in agreement with (Iyenagba& Othman, 2012). Report by (Kingsley, 2010) also holds that RHA fired at 900^0 attained significant crystallinity with reflections or sharp peaks of different phases of SiO_2 in their XRD pattern. The particle size calculated from Debye- Scherrer formula was 30.34 nm.

The particle size value fits well in the range 20 – 30 nm reported by Young *et al.* (2008).

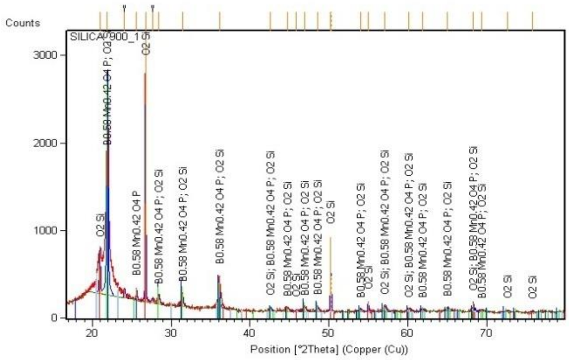

Fig. 2: X-ray diffractogram of rice husk ash

FTIR characterization

Figure 3 shows FTIR result of aerogel heated at 900^{0}C. There were characteristic bands of silica aerogel detected. The absorption at 817.85 cm^{-1} belongs to bending vibration of O –Si –O. The band 946.12 cm^{-1} is associated with the C –H out-of-plane bending vibration while the band at 1090.78 cm^{-1} is assigned to C –O as a result of the alcohol and other impurities like ethers, esters, carboxylic acid and anhydrides. Absorption at 1383.97 cm^{-1} is ascribed to the C –H bending vibration of –CH_3, and that at 1634.73 cm^{-1} is attributed to the C=C mode with no interpretatively useful vibration. The band 2103.44 cm^{-1} is also associated with the C=C mode probably due to the alkynes. The 2772.76 cm^{-1} band can be traced to the C –H mode; while absorption at 2847.03 cm^{-1} is due to the C –H stretching vibration. And 3469.09 cm^{-1} is associated with O –H group due to H –bonding. Similar 3469.09 cm^{-1} band is reported by Kien-Who *et al.* (2014) and Azedeh*et al.* (2012) at 3500 cm^{-1} to be attributed to the stretching vibrations of O –H bonds in water molecules, bonded by hydrogen bonds or OH groups present in organic compounds.

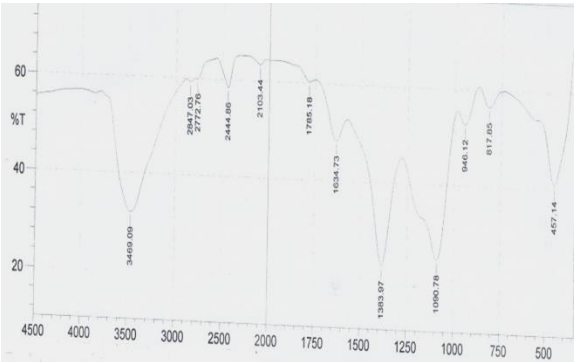

Fig. 3:FTIR spectrum of silica aerogel

Surface morphology

The nature and form of the samples were examined using a scanning electron microscope. Plates 5 – 7 present the SEM micrograph of the prepared samples. Plate 5 reveals the fused solid nature or honey comb of the RHA. Plate 6 shows the white parts in the surface of the gel the black parts as pores. And Plate 7 shows the compact nature of silica aerogel.

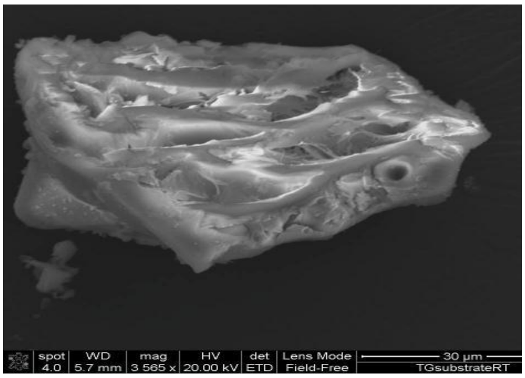

Plate 5:SEM micrograph of rice husk ash

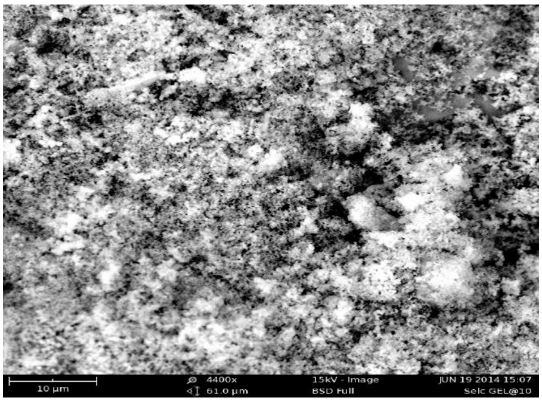

Plate 6:SEM micrograph of silica gel

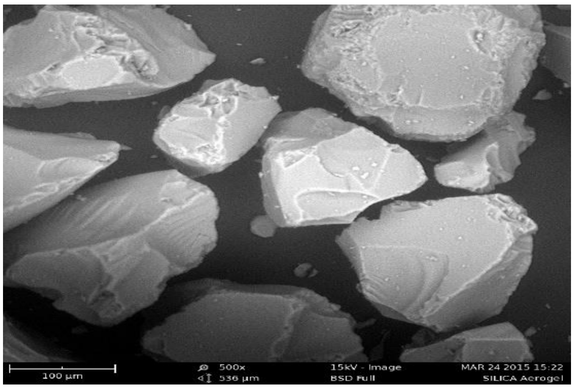

Plate 7:SEM micrograph of silica aerogel

Conclusion

Rice husk, an important agricultural waste, rich in silica can be used for a number of applications. The paper has demonstrated that thermally treated rice husk yields ash that can be processed under controlled techniques to obtain silica aerogel. The pure SiO_2 obtained was 98.32 by Wt%. X-ray diffraction analysis of the RHA revealed crystalline structure with average article size of 30.34 nm. The bulk density of aerogel was found to be 0.58 g/cm^3 and porosity of 71.0%; while its refractive index was 1.122.

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