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Synthesis and characterization of nanosized-silica gels formed under controlled conditions

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ABSTRACT

Silica gel has been synthesized by the refluxing of rice husk ash with 1 M NaOH and subsequently adjusting the pH using 1 M H_2SO_4. The high purity of the silica gel has been found to be dependent on: (i) reflux time, (ii) water loading by addition of boiling DI water to the silica gel prior to titration with 1 M H_2SO_4 and (iii) rinse time on removal of impurities prior to drying. The surface area, pore size and volume of the silica gel were measured; XRD peaks of Na_2SO_4 impurity were absent after rinsing >4 times. FTIR spectra showed that all the silica gels made by different schedules had a similar functional composition. The advantages of the present synthesis route are (i) a cost reduction due to the absence of pre-treatment for the rice husks before calcination below 700 °C, and (ii) the formation of a pure high surface area mesoporous amorphous silica gel.

1. Introduction

Rice husk is an abundantly available waste material in rice-producing countries where there is a need for its disposal or utilization. It would be of benefit to the environment to recycle the waste to produce eco-materials having a high end value. The white ash obtained from its combustion or calcination at relatively moderate temperatures produces a main residue containing silica (SiO_2) in the form of an amorphous phase, together with small amounts of impurities of metallic oxides [1–5]. Amorphous silica powder is a basic raw material that is widely used in industries associated with ceramics, rubber, electronics, catalysis, pharmaceutics, dental materials and other materials. The small particle diameter and high surface area of the ultra-fine silica powders give rise to many technological applications [3]. It has been reported previously that pure silica can be obtained from rice husk ash by various procedures; these include fluidized bed [1], non-isothermal decomposition in oxidizing atmospheres [4], chemical pre-and post-treatment using acid and base solutions [5], pressurized hot-water treatment processes [6], and carbonization and combustion [7]. However, the relatively high cost of these preparation routes has limited the wider application of the product and often the resultant silica has insufficient moisture adsorption. The beneficial form of silica able to adsorb moisture is silica gel (SiO_2 gel), which can be synthesized as a precursor gel directly from rice husk ash. In medical applications, the use of SiO_2 gel as a drug delivery agent is increasing because of its highly porous structure which enables large amounts of the active ingredient to adsorb onto the surface. Previous reports show that SiO_2 gels can be prepared by the sol–gel method using a variety of starting materials as the Si source, for example (i) rice hull ash or rice husk ash [8,9] and (ii) tetraethylorthosilicate (TEOS) [10–13]. SiO_2 gel made from TEOS is more expensive than that sourced from rice husk ash and additionally TEOS is a hazardous chemical. It has been reported that SiO_2 gel made by the sol–gel process using many steps involving chemical treatment and refluxing rice husk ash made it possible to process a high surface area product [9].

In the present work, conditions for synthesis of high purity of SiO_2 gel by a sol–gel method have been optimized and the range of parameters affecting particle size, surface area and pore structure have been investigated and discussed. The synthesized SiO_2 gel is aimed for applications in the medical industries which require materials having consistent high purity, high surface area, together with controlled size and structure.

2. Experimental methods

2.1. Preparation of silica gel

A mixture of rice husk ash (10 g) calcined at 650 °C for 6 h and 1 M NaOH (320 cm^3) was heated under reflux for 3, 5 and 9 h. The reflux process was considerably modified in comparison with previous studies [8,9]. In our study, longer time periods were used for the reflux process and the washing process was systematically repeated. The following procedures were carefully performed to obtain a final product having the necessary high purity. The reaction mixture was filtered via a Whatman filter paper using a vacuum pump to assist.

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Carbon residue was washed in boiled water (200 or 400 cm^3). The filtrate, a sodium silicate solution, was cooled to room temperature and slowly titrated against 1 M H_2SO_4 with constant stirring. The pH of the solution was monitored and the titration stopped once the pH reached 7. When the gel formed from the sol, it was aged for 18 h. After aging, the gel was gently broken and the slurry was centrifuged for 5 min at 6000 rpm. Distilled water (400 cm^3) was added to the gel, and the mixture gently swirled and centrifuged. The washing step was repeated 2, 4, 6 and 8 times. Subsequently, the gel was spread on a glass dish and dried in a vacuum oven at 80 °C. The agglomerated silica gel was then ball-milled using ZrO_2 balls in plastic containers.

2.2. Characterization

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the as-received rice husk was undertaken using a simultaneous thermal analyzer (STA), Netzsch STA 449C, Germany. The measurements were carried out using 21.864 mg of sample in an oxygen atmosphere with a heating rate of 10 °C/min over the temperature range of 30–1000 °C. The thermal analysis data was recorded using alumina as an inert reference material. To study the phases present, each of the products was characterized by X-ray diffraction (XRD) using JEOL, JDX-3530, Japan with Cu K_α radiation. The pattern was acquired in the 2θ range 5–90°. Metal oxides in the rice husk (RH), rice husk ash (RHA) and silica gel (SiO_2 gel) were identified using a X-ray Fluorescence Spectrometer (XRF), a Phillips, PW-2404, Netherlands. All samples for XRF analysis were prepared by pressing 5.0 g powder with 1.0 g of boric acid (H_3BO_3) binder.

A Flowsorb II 2300, Micromeritics, USA, was used to determine the specific surface area. The SiO_2 gel samples were degassed in an oven at 250 °C for 660 min and the pore size determined using a Quantachrome Autosorp-1. Infrared spectra of the samples were collected on a FTIR Spectrometer, (System 2000, Perkin-Elmer, England), at 20 °C using the standard KBr method. The spectra of functional groups in the SiO_2 gel were recorded over the wavelength region of 4000–400 cm^{-1}. The microstructure of each of the synthesized SiO_2 gels was observed using a scanning electron microscope (SEM), (JSM 5410, JEOL, Japan) at 20 kV. All samples were placed on brass cylinders (stubs), dried in a vacuum chamber at room temperature and coated with a thin gold layer. Transmission electron microscopy (TEM), (JSM 2010, JEOL, Japan) was used to observe the fine microstructure, particularly the size and pore characteristics of the silica gel particles. To prepare the TEM sample, small amounts of the sample powder were dispersed in ethanol and allowed to settle on a carbon film supported by a 200 mesh Cu-grid.

3. Results and discussion

3.1. Property determination

3.1.1. Thermal analysis

10 g of rice husk ask can produce approximately 7.31 g of SiO_2 gel giving a 73.10% yield. Fig. 1 shows TGA and DTA data profiles of the rice husk. Four stages of weight loss were apparent, as can be seen in the TGA profile. The first step -11.56% occurs over the temperature range ~30–140 °C and involves removal of moisture, the second step in the range of 140–170 °C is constant and the third and fourth steps −47.05% and -21.25% which take place in the temperature range 175–380 °C and 380–550 °C, respectively, involve organic compounds (hemicellulose, cellulose, and lignin) and their decomposition. The residual ash is 19.60% after heating above 550 °C and consists of SiO_2. The DTA profile reveals two exothermic peaks occurring over two temperature ranges, 250–380 °C and 380–525 °C. These two peaks show decomposition of the organic compounds; hemicellulose, cellulose and lignin. A summary of TGA/DTA results is listed in Table 1.

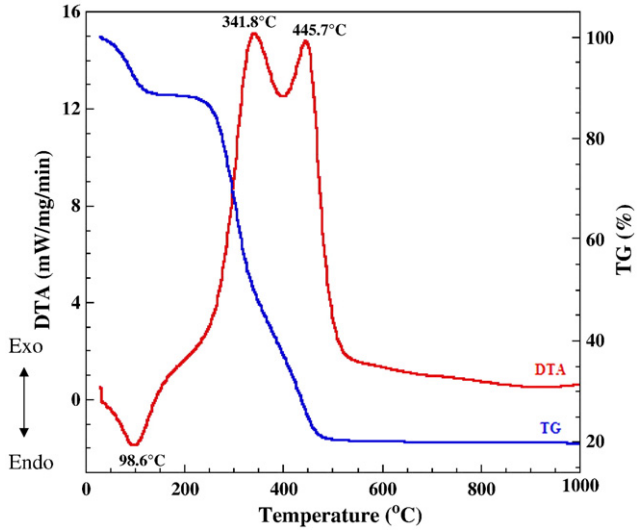

Fig. 1. TGA/DTA profiles of the rice husk used in this study.

3.1.2. Phase present

Fig. 2 illustrates the XRD patterns of the RH, RHA and SiO_2 gel. As seen in the figure, the RH profile shows a characteristic peak of SiO_2 (JCPDS number of 29-0085) and consists of two broad peaks at 10° and 15°. The peak at 2θ = 15° has disappeared after calcination at 650 °C for 6 h and as yet cannot be attributed to a specific species. Patel et al. reported that the temperature of carbonization is preferably held below 700 °C to avoid any transformation of the amorphous phase to a crystalline form [14]. It has been found that reheating the ash to remove carbon residues takes a relatively long period of time and somewhat higher temperatures, with the consequence that any amorphous silica is then converted to a crystalline form. However the structure of silica present in the ash treated at 700 °C for 6 h remained essentially amorphous [15]. The XRD patterns of SiO_2 gels obtained using RHA refluxed with 1 M NaOH for 5 h, titrated with 1 M H_2SO_4 and rinsed 6 times did not show a peak at 2θ–10° and 15°. Thus it is apparent that the sol–gel method, in conjunction with lower temperature calcination, is still able to remove any remnant organic matter. From the SiO_2 gel spectrum, it is clear that we are able to synthesize a relatively pure SiO_2 gel by following to this procedure.

3.1.3. Chemical composition

Table 2 indicates that K_2O, MgO and MnO_2 were detected in RHA and were also present but at lower concentrations than in RH after calcination in air. Fe_2O_3 and Al_2O_3 could not be detected in all samples. The SiO_2 gel samples contained CaO, SO_3, MgO, P_2O_5, and MnO_2, below the limit of quantification <0.1 mg g^{-1}. Remnant Na_2O is present in the SiO_2 gel due to the refluxing of the SiO_2 gel with 1 M NaOH during processing, which resulted in the samples retaining Na^+ ions. These very low level concentrations can be explained by the leaching of

Table 1
TGA/DTA of the rice husk used in this study.

Stage	TGA		DTA		Decomposition
	Temperature range (°C)	Weight loss (%)	Max. peak temperature (°C)	Peak character	
1	30–140	11.56	98.6	Endotherm	Moisture/water
2	140–175	~0.00	–	–	–
3	175–380	47.05	341.8	Exotherm	Hemicellulose, and cellulose
4	380–550	21.25	445.7	Exotherm	Lignin

+++ The residual weight percent is 19.60% and after heating above 550 °C, when the ash consists of SiO_2.