

Sol-Gel-Derived Porous Silica: Economic Synthesis and Characterization

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ABSTRACT

Porous silica was synthesized via the sol-gel process using clay obtained locally from Ijero-Ekiti in Ekiti State, Nigeria and compared with silica synthesized under similar conditions from sodium metasilicate (Na_2SiO_3) obtained commercially. The clay was initially refluxed with sodium hydroxide (NaOH) for 2 hours to extract SiO_2 to form Na_2SiO_3 , which was subsequently hydrolyzed to form a gel. The gel obtained was washed with deionized water to get rid of impurities, dried and calcined at 800°C for 3 hours. The obtained silica powders were characterized using atomic absorption spectrophotometer, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results showed that the vibrational modes and diffraction patterns of the silica derived from commercial Na_2SiO_3 and that prepared from clay were similar containing pure amorphous SiO_2 . The morphology of the commercially obtained silica showed better arrangement of particles and exhibited slightly lesser porosity (62.4%) compared to that derived from clay which had a porosity of 65.5%. The result indicates that clay has a potential for use as an environmentally safe and economic starting material for preparing porous silica instead of high quality precursors.

Keywords: Clay; Sodium Metasilicate; Economic; Porous Silica; Environmentally Safe

1. Introduction

Porous silica is used in many fields including biotechnology, biomedical sciences, selective separation and catalysis [1,2]. Unlike conventional glass, which is a viscous fluid that results from the fusion of SiO_2 at high temperature, sol-gel-derived silica is obtained at mild conditions [3] compatible with the stability of most bioactive compounds. The sol-gel process is capable of generating materials with controlled surface properties and pore structures between 1 - 500 nm [4-7]. The matrix of the silica thus formed can be exploited for immobilization of biomolecules or cations, inorganic membranes and support for catalysts [6-9].

Silica polymer networks may be obtained by hydrolysis and condensation reactions of silica precursors such as tetraethyl orthosilicate (TEOS). By controlling synthesis conditions carefully, the sol morphology can be directed towards weakly branched polymeric systems or to particulate systems [7]. Important process parameters include water content, the solvent, the catalyst used and its concentration and type of alkoxide used [4,10,11].

Several methods, most of them based on TEOS as starting material have been used to prepare porous silica. The most popular is the sol-gel synthesis proposed by

Stöber *et al.* [12] which is based on hydrolysis and condensation of highly reactive silicon alkoxide precursor at low temperature. Consequently, silica particles with various characteristics were prepared by ammonia-catalyzed reactions of tetraethyl orthosilicate (TEOS) with water in low molecular weight alcohol [12,13]. Due to high cost, applicability of other precursors has been investigated. Thus, different types of silica sources have been used, such as sodium silicate [14,15] and even environmentally safe and renewable resources, like rice husk ash [16,17], rice hull ash [18] and rice straw ash [19] have also been exploited.

In continuation of the search for a cheap and environmentally safe silica source, the work herein investigated the synthesis of porous silica from clay and sodium metasilicate under similar conditions for the purpose of comparing their physical and morphological characteristics.

2. Materials and Methods

2.1. Materials

The chemicals used were sodium metasilicate (Na_2SiO_3), (Sigma-Aldrich) with composition SiO_2 24.9 and Na_2O 20.9 wt% respectively, clay from Ijero-Ekiti in Nigeria

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having composition (as previously analyzed by Olasupo and Omotoyinbo [20]) as shown in **Table 1** and sulphuric acid (H₂SO₄), (Fluka, Germany).

2.2. Preparation of Porous Silica from Sodium Metasilicate (SS)

Sodium metasilicate (5.0 g) was stirred in distilled water (10.0 ml) to give a clear solution. Thereafter, 10.0 ml of 2 M H₂SO₄ was added dropwise to the mixture under magnetic stirring at room temperature for about 2 hours to form a gel. Deionized water was added successively to the gel to wash and remove sodium sulphate (Na₂SO₄). Complete removal of sodium ions was indicated by absence of white precipitate when the liquid from the last filtration was tested with dilute lead(II) ethanoate solution. The washed gel was dried in an oven at 120°C for 1 day, calcined at 800°C for 3 hours in a furnace with a heating rate of 10°C/min and thereafter milled to form powders and then labelled as SS.

2.3. Preparation of Porous Silica from Clay (CS)

The as-received potter's clay was dried in the sun, following which it was ground into powder in a ball mill and sieved through a 100 µm to remove oversize particles. The obtained clay (10.0 g) was refluxed in 1 M NaOH solution (200.0 ml) for 2 hours, then allowed to cool before filtering to remove the residue which contained Al(OH)₃ as major impurity. The filtrate obtained was evaporated to dryness to give as residue sodium metasilicate, Na₂SiO₃ (5.0 g). The basic sodium metasilicate was dissolved in distilled water (10.0 ml). The solution was hydrolyzed with 2 M H₂SO₄ (20.0 ml) and subsequently treated the same way as in section 2.2 above to afford the silica powder which will henceforth be called CS.

3. Characterization

X-ray diffraction (XRD) analysis was carried out in the 2θ range of 10° - 80° and 5° - 120° using Xpert PRO PANalytical diffractometer employing CuKα radiation

Table 1. Mineralogical composition of Ijero-Ekiti clay.

Minerals	Amount (%)	Oxides	Composition (%)
Kaolinite	72	SiO ₂	63.3
Quartz	22	Al ₂ O ₃	16.5
Feldspar	4	Fe ₂ O ₃	5.8
Illite	2	CaO	1.7
		MgO	0.6
		LoI	12.5
		Others	0.8

LoI = Loss on ignition.

(0.154060 nm) source operated at 40 kV and 40 mA. Fourier transform infrared spectroscopy (FTIR) studies were carried out using Buck Scientific 500 Infrared spectrophotometer with KBr as reference in the wave number range of 600 - 4000 cm⁻¹. Atomic absorption spectroscopy Perkin Elmer A Analyst 200 was used to determine residual amount of sodium ions (Na⁺) present in the silica networks. Morphological characterization of the samples regarding the particles and pore sizes distribution were performed using a SEM (EVO/MA10) at an accelerating voltage of 10 kV.

The bulk densities, ρ_b of the silica particles were measured from their weight to volume ratio using the formula

$$\rho_b = M/V \quad (1)$$

where, M is the mass of the sample measured with a microbalance (10⁻⁵ g accuracy), and V is the volume measured by filling the silica particles in a column of known volume [21].

The porosity, $P(\%)$ was estimated using the relationship [22]

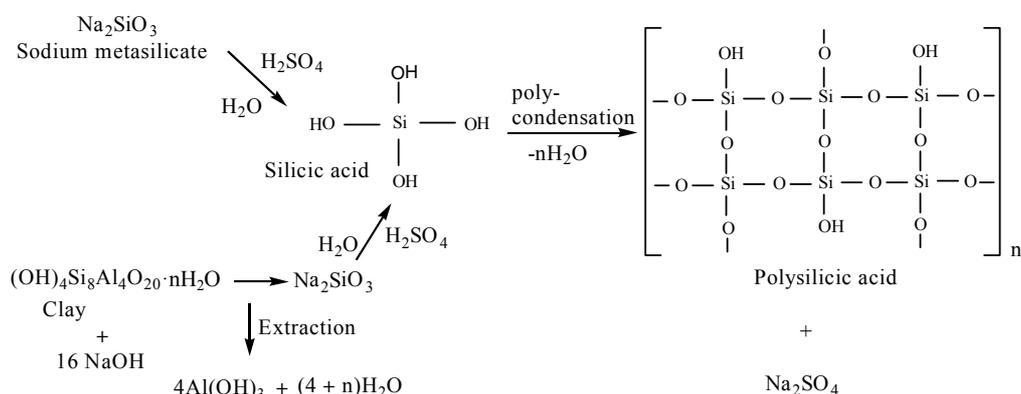
$$P = (1 - \rho_b / \rho_p) \times 100 \quad (2)$$

in which ρ_p is specific density assumed to be 2.0 g·cm⁻³ for amorphous silica particles based on the spherical model (a typical average density of silica prepared via wet-synthesis conditions [23]).

4. Results and Discussion

4.1. Hydrolysis and Gelation

Acidic hydrolysis of sodium metasilicate (Na₂SiO₃) gives silicic acid [24] in solution. Sodium hydroxide is reacted with clay to initially afford sodium metasilicate in a strongly basic medium. The water glass obtained from the basic reaction is similarly hydrolysed to silicic acid which undergoes condensation to disilicic acid and further reaction to a polycondensed hydrogel [24] as shown in **Scheme 1**. Thereafter, the gel obtained from both precursor compounds were subjected to multiple washings [25] with deionised water to free the gel of sodium sulphate formed during hydrolysis that is trapped in the pores of the gel network. During aging, the 3-D framework of the silicate glass continues to grow and becomes more rigid by contracting and expelling liquid water present inside the pores [26]. Drying is important as it modifies the gel characteristics and involves two steps [27]. During the first step, the pores are emptied; the capillary gradient induces the liquid flow along the pore walls, towards the external surface where it evaporates. At the interior, the pores are still filled with liquid, while the air enters the most external pores, which can cause the opacity of gel. The pressure capillary gradient decreases gradually, the flow is increasingly slower then



Scheme 1. Hydrolysis and polycondensation of sodium metasilicate and clay.

stops. In the second step the remaining liquid can then leave the gel only in gas form, with vapour diffusion towards the surface. After drying at 120°C, the porous gel contains a small quantity of liquid trapped in the pores. Calcination at high temperature further removes absorbed water trapped in the pores.

The efficiency of deionised water washings to free the gel from sodium sulphate was monitored by atomic absorption spectroscopy (AAS) analysis of the silicas obtained after drying. The result indicated that Na⁺ decreased from 36.5% (on the basis of stoichiometry) [25] to 1.6% in the SS-based silica and to 2.1% in the CS based silica.

4.2. Bulk Density and Porosity

The silica obtained from SS and CS after calcination were found to have bulk density of 0.752 and 0.690 g cm⁻³ respectively. The difference may be due to better packing of the 3-D framework in the SS as a result of more efficient removal of the interfering Na⁺ from successive deionized water washings of the gels [28]. Their bulk densities as expected had influence on their porosity, as SS and CS exhibited 62.4% and 65.5% respectively.

4.3. FTIR

The FTIR spectra obtained for the SS and CS-based silicas respectively are characterized by a broad band centred around 3400 cm⁻¹ and a smaller signal around 1630 cm⁻¹ that corresponds to O-H absorption band [29,30] as shown in **Figures 1(a)** and **(b)**. Furthermore, a diagnostic Si-O-Si asymmetric stretching vibration is centred on 1132 cm⁻¹ [31,32] and the absorption signal at 920 cm⁻¹ is assigned to the stretching vibration of silanol groups on the surface of the amorphous solid [33].

4.4. XRD

The XRD spectra of the SS and CS powders obtained are shown in **Figures 2(a)** and **(b)** respectively. The diff-

raction patterns are similar for both samples which appear as broad bands with reflection at $2\theta = 22^\circ$ indicating that the materials are amorphous and composed of SiO₂ [34-36]. There are no additional peaks observed in both spectra. This result indicates the absence of impurities in the gel networks after the deionised water washing removal of Na₂SO₄ formed during the gelation reaction (**Scheme 1**), the extent which was confirmed earlier with AAS.

4.5. SEM

The particle sizes of the silicas measured by SEM are presented in the micrographs shown in **Figure 3**. The average particle size of SS was 353.95 nm, **Figure 3(a)** while that of CS was 755.35 nm, **Figure 3(b)**. The difference in particle sizes in the two samples may be the result of agglomeration [37] which is higher in CS than SS. This fact is more evident in **Figure 4** where in the micrograph of SS, **Figure 4(a)**, the particles appear as discrete with a few agglomerates, whereas the particles of CS as seen in the micrograph shown in **Figure 4(b)**, appear to adhere to each other forming aggregate of particles which results in irregular arrangement when compared to SS. It has been proposed [38] that the initial particle size distribution, polydispersity, concentration of particles, viscosity of the continuous phase, Van der Waals forces of attraction, and hydrodynamic conditions govern the extent of inter-particle collisions, aggregation and the temporal evolution of the average diameter of aggregates. The morphology of CS therefore appears to be more porous than that of SS which agrees with the porosity values earlier obtained. According to studies [39], porosity arises from the assumed packing of primary particles in the agglomerates.

5. Conclusion

Porous silica has been successfully synthesized via an

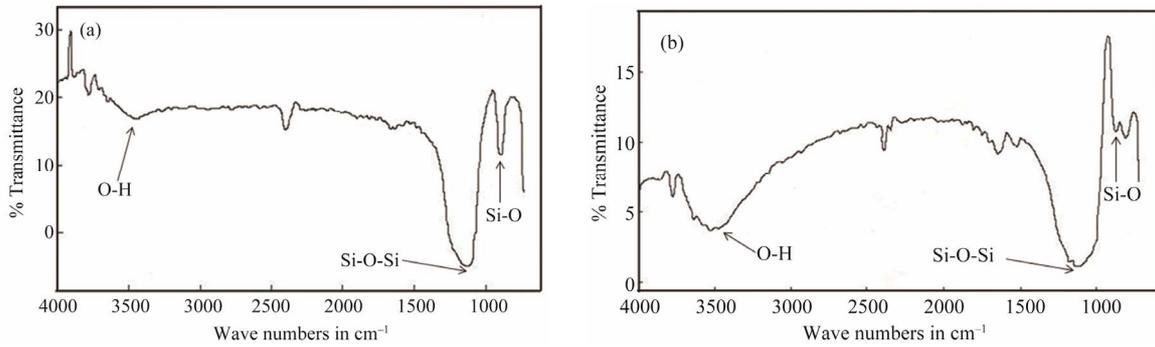


Figure 1. (a) FTIR spectrum of SS-based silica; (b) FTIR spectrum of CS-based silica.

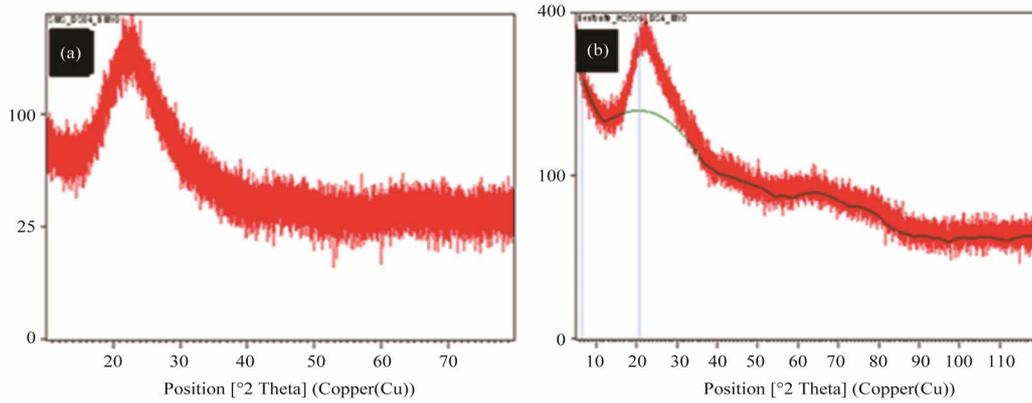


Figure 2. XRD patterns obtained from (a) SS and (b) CS powders.

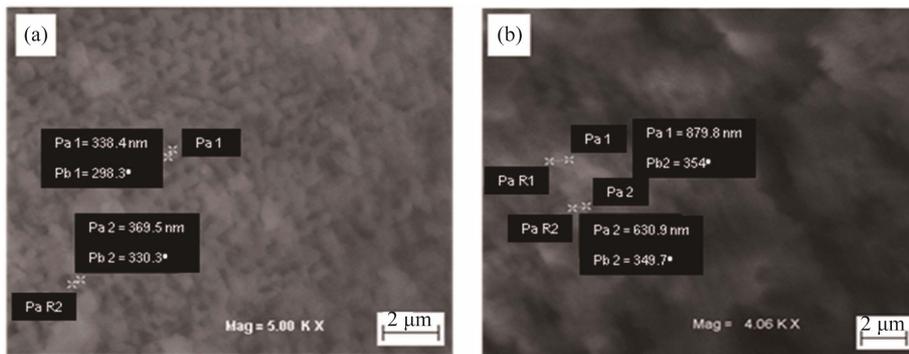


Figure 3. SEM micrographs of samples (a) SS and (b) CS showing particle sizes measured at different positions: Pa 1 and Pa 2 at positional angles of Pb 1 and Pb 2 respectively.

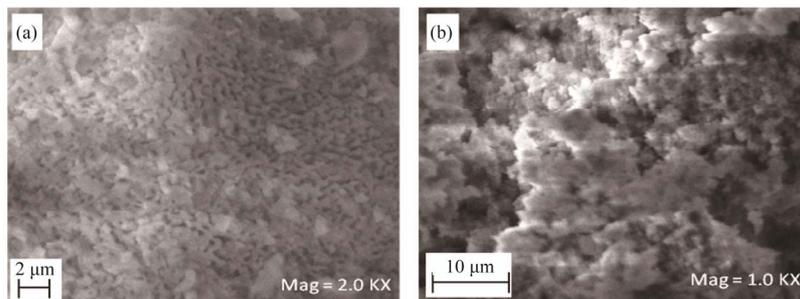


Figure 4. SEM micrographs showing the porous morphology of the sol-gel-derived silicas. It can also be seen that SS, (a) contains better packed particles than CS, (b).

economic route using a Nigerian clay. Results obtained from FTIR, XRD and SEM characterization showed that the material possessed properties comparable to silica obtained from commercial sodium metasilicate prepared under the same conditions. It is therefore concluded that clay which is cheap and widely available in Ekiti State, Nigeria may be a potential starting material for commercial scale preparation of porous silica.

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