Sol-gel preparation and synthesis of mesoporous Silica using de-ionised water as Solvent and Poly (ethylene-glycol)-block-poly(propylene-glycol)-block-poly(ethylene-glycol) as source of Micelle

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Abstract— Sol-gel method is a vital wet chemical method for the preparation of gels and other crystalline and non crystalline materials. The method was carefully utilized to synthesize Mesopores with average particle size of 661nm and average distance of 1µm. De-ionised water as compared to ethanol or other polar and non polar solvent was applied to Tetra ethyl ortho-silicate (TEOS) to form the alkoxide and poly(ethylene-glycol)-block-poly(propylene-glycol)-block-poly(ethylene-glycol) was used to form the micelle required for template building. Scanning electron microscope (SEM), Energy dispersive X-ray (EDX) and X-ray Diffraction (XRD) were used to investigate the independent elements constituting the mesopore architectures. The architecture constituting the mesopore framework was confirmed to solely depend on the type of solvent used and on the P^H of the solution. High ordered structure mesopores of the Santa Barbara Amorphous -15 (SBA/15) was confirmed and synthesized to be widely utilized in catalysis, oil refining, water treatment, drug delivery and advanced nano-technology.

Keywords: Alkoxide, Architectures, Mesopore, SBA/15, Template.

1.0 INTRODUCTION

Designing higher-order inorganic matter with architectural assemblies to serve as framework for catalytic reaction is a key challenge in catalysis [1]. Mesoporous materials have attracted huge interest to the catalyst scientist because of the properties they exhibit such as, low density, large specific area and nano structural spheres ranging from 10-50nm [2]. These properties provide the catalyst scientist the ability to tailor Mesoporous materials into useful products utilized in, electrical Engineering, drugs synthesis, confine space catalysis and bio-molecular separation [3]. Silica is a very important natural occurring material. It is found in minerals and in plants such as, Quart, bamboo and barley [3]. The property of Silica is extensively studied with very rich literature available. However, its high surface area and thermal stability makes it a potential for technological applications in catalysis and mining. Silica Mesoporous architectural frame loaded with metals, such as Cobalt, Nickel and Iron have been widely studied using processes such as Fischer-Tropsch and Gas reforming [4]. Cobalt, however exhibits properties promoting heavy un-branched hydrocarbons, oxygenated products, low sintering, high selectivity and product optimization at low temperature [4]. Therefore synthesis of stable supported Cobalt catalyst is envisaged to reduce methane production and increase gasoline yield by this means improve olefinic contents [4], [5].The sol-gel method which this work reports is a vital chemical technique used to synthesize inorganic materials and inorganic-organic hybrids via a wet chemical process. The sol–gel reaction was utilized to synthesize silica supports with mesopores as high as 200-661nm in this research. Inorganic salts with metal-oxygen bonds, namely metal alkoxides M(OR)n or oxoalkoxides MO(OR)n (R=saturated or unsaturated organic group, alkyl or aryl) are used as precursors.

Sol-gel chemistry with metal alkoxides is best illustrated below in Reaction 1.0.

$$\boldsymbol{Hydrolysis}:\ \boldsymbol{M-OR+H_2O=M-OH+R-OH}$$
$$\boldsymbol{Condensation}:\boldsymbol{M-OH+XO-M=M-O-M+XOH} \quad (1)$$

Where X-H or R (Alkyl group)

To prepare gels of high quality using this method, proper control and monitoring of a list of parameters, such as the nature of the precursors, mixing ratios of reagents, temperature, P^H, aging and drying of the gel must be attained [6]. The effective control and monitoring of these parameters have resulted to the development and synthesis of materials with high pore volumes and surface area such as the :Mobil Crystalline material (MCM) and SBA that anchors recent developments and thereby finding wider applications in catalysis, drug delivery, imaging and currently nano-technology [7].

2.0 EXPERIMENTAL

2.1 Materials

Chemicals and reagents used in the preparation of the mesoporous structure were of the highest analytical grade.

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Poly(ethylene-glycol)-block-poly(Propylene-Glycol) block-Poly(Ethylene-Glycol) known as **Pluronic (P-123)** is a tri-block co-polymer of Aldrich Chemicals, USA.

2.2. Synthesis of Mesoporous Hollow Silica Spheres

4g of PEG-PPG-PEG and 120g of De-ionised water was added into a Poly-ethylene bottle. The mixture was placed into a glass bowl filled with distilled water and the solution was then placed on a hot plate regulated at 60 ^{0}C with a magnetic stirrer added to stir the solution at approximately 540 rpm/min as reported by Zhao et al [8]. After 6 hours, a clear solution was observed confirming the complete solubility of PEG-PPG-PEG by De-.ionised water.

To control flocculation 20ml of HCl (37%) was added to the solution and 10 mins later, 9.25ml of Tetra-ethyl-ortho-silicate (TEOS) was added slowly dropping 25-30 drops/min under vigorous stirring for 20 hrs. A White precipitate was observed.
The white precipitate was transferred to an oil bath regulated at 95 ^{0}C for 24 hours to age without stirring. The white solute precipitate was then filtered, washed sufficiently with distilled water to remove the template (P123) from the pores of the mesoporous channels and afterwards the white solute powder was dried at 60 ^{0}C for 24 hours. The white powder was calcine at 400 ^{0}C under steady state for 6 hours increasing the temperature at 10 ^{0}C/ min for 6 hours and cooled from 550 ^{0}C to 60 ^{0}C at 10 ^{0}C/ min. The calcine powder was placed on a hot plate and boiled for 2hrs at 105 ^{0}C stirring gently. Finally, after 2 hours, the mixed solution was filtered, dried and measured to determine its weight.

2.3. CHARACTERIZATION TECHNIQUE:

2.4 Scanning Electron Microscope (SEM)

The SEM analysis of the sample was conducted using a Hitachi 3400n instrument at a voltage of 30kV. The powdered specimen of the sample was coated with gold to form a conductive layer and loaded on a carbon stub to evaluate the surface particle property of the catalysts loaded.

2.5 X-ray Diffractometer (XRD)

The Siemens Diffractometer crystallographer was used to determine the properties of crystals and diffraction pattern using Cu-Kα radiation at room temperature.

2.6 Energy dispersive X-ray spectroscopy (EDXS)

Hitachi 3400n was utilized to measure the elemental composition and to charactersise the specimen with minimum measurement of 4-5 micron-meter (μm).

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3.0 DISCUSION OF RESULT

3.1 SEM Result

The SEM images of samples prepared using the Sol-gel method before and after calcinations are shown in Fig. 1.0 and 2.0 respectively. Fig 1.0 is observed to be spherical and irregularly packed together as compared to sample B. This irregularity observed from the morphology of sample A, might be as a result of loss of water during hydrolysis and removal of P123 templates during calcinations compared to sample B observed to have a uniform arrangement of spheres as a result of the restructuring of silanol groups.

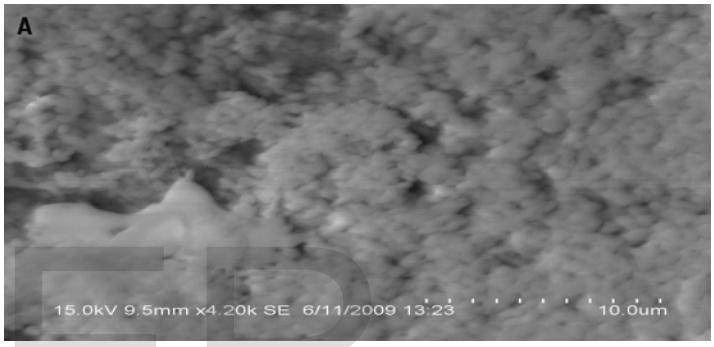

Figure 1.0 SEM Sample of non-calcine sample

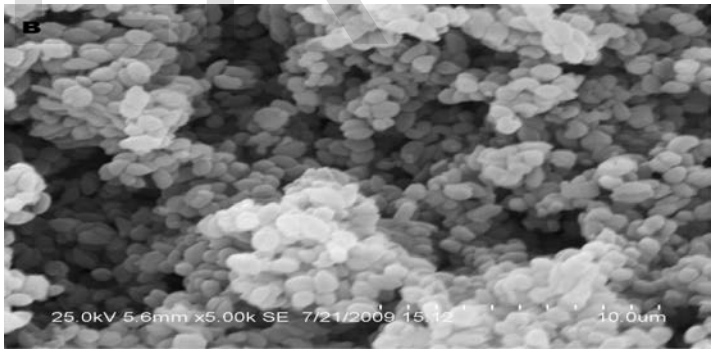

Figure 2.0 SEM Sample of calcine sample

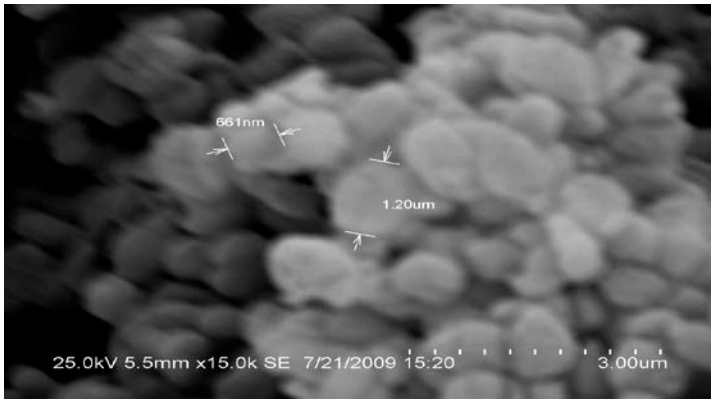

Figure 3.0 SEM micrograph of calcine sample with 661nm

Fig 3.0 shows the SEM micrograph of a calcine sample with average particle size and distance of 661nm and 1.2µm respectively. The sample prepared via the Sol-gel method is therefore a mesoporous material with average particle size of 661nm and will provide a large particle and pore volume of the SBA/15 as reported by Augustus et al [9].

3.2 X-ray Diffractometer (XRD)

Low-angle XRD is a key method for the identification of the meso-structures. Fig 4.0 shows the low angle XRD patterns of SBA-15 samples that could serve as catalyst vehicles for Cobalt, Nickel and Iron loadings. Apparently, the XRD patterns show well-resolved peaks at low angle 2θ region, characteristic of SBA-15 [9, 10]. Peaks, indexed as (100), (110), (200) reflections associated with p6mm hexagonal symmetry, reveal hexagonally arranged mesopores over long range. The following reflections at 2θ for peaks (100) 1.0nm, (110) 1.66nm and (200) 1.84 respectively were observed. This reflections confirms the architectural frameworks same as SBA/15 reported by Xiang et al. [1]

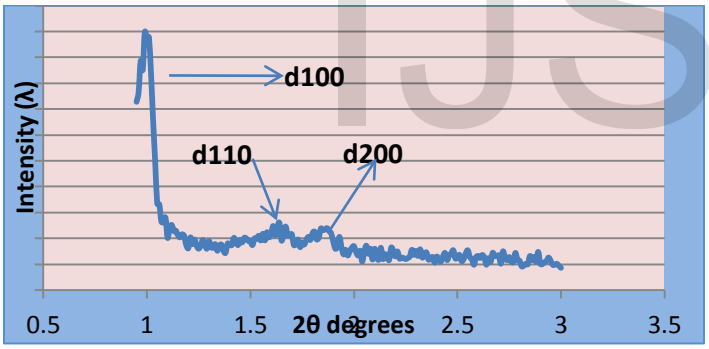

Figure 4.0 XRD of Sample synthesized

3.3 Energy Dispersive X-ray Spectroscopy (EDXS)

The EDX measures the elemental chemical composition constituting the Mesoporous on a selected radii surface of Mesoporous Silica (SBA-15). Approximately 4-5 µm of the specimen prepared was analyzed and the various compositions of elements are shown Table 1.0 and Figure 5.0 respectively. The various compositions in percentages (%) of elements constituting the Mesoporous silica was confirmed as C, O, Si, S in different percentages as shown in Table 1.0

Table 1.0 Elemental composition of Mesoporous structure

Element	Weight%	Atomic%
C (K)	16.19	23.63
O (K)	51.08	55.97
Si (K)	32.45	20.25
S (K)	0.27	0.15
Total	99.99	100

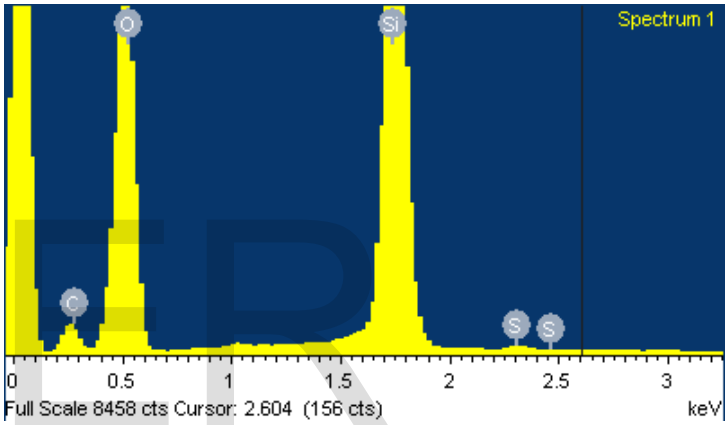

Figure 4.0 EDX graph spectrum of the sample

CONCLUSION

Among the existing methods available to researcher to prepare gels, sol-gel is widely utilized because of the ability of researchers to tailor properties such as: variability, low temperature and purity of the gels. These properties were utilized to carefully synthesize a mesopore framework of silica with average particle size of 661nm and distance of 1 µm as reported. A mesopore of the order of SBA/15 was synthesized and confirmed after the characterization techniques.

The structure synthesized with mesopores particle size as high as 661nm and average distance of 1 µm can be used as a catalyst vehicle in drugs production and delivery, chemical operations such as refining, water treatment and when loaded with metals such as Nickel, Cobalt and Iron.

REFERENCES

[1] Xiang Wang, Fabrication of Mesoporous Silica hol low spheres, using tri-block co-polymer PEG, PPG-PEG as template: Journal of Non-crystalline solids. (2010) 898-905.
[2] B. Xie, H. Shi, G. Liu, Y. Zhou, Y. Wang, Y. Zhao, D. Wang, Chem. Mater. 20 (2008) 3099
[3] A.C. Yanes, J.D. Castillo, M. Torres, J. Peraza, V.D. Rodríguez and J. Méndez-Ramos (2004), Appl. Phys. Lett., 85, 2343–234.
[4] Ayiya,B.B. Preparation and characterization of Cobalt catalysis on Mesoporous silica via Sol-gel method. Teesside university, Middlesbrough, U.K. (2009). (Unpublished)
[5] R.G. Rodriguez and J.A de los Reyes, Preparation and characterization of Mesoporous titanium silica and Zirconia Silica mixed Oxides. Superficies y Vacio (19) (2) ,(2006) 1-6
[6] Junhua Li et al. Hollow mesoporous silica sphere supported cobalt catalysts for F–T synthesis. Catalysis Today 148, (2009) 148–152.
[7] Koichi Kajihara. Recent advances in sol–gel synthesis of monolithic silica and silica-based glasses Journal of Asian Ceramic Societies 1 (2013), 121–133.
[8] Xinyuan Zhao, C. M. Wei, L. Yang, and M. Y. Chou. Photocatalytic Activity of Nanosized $ZnWO_4$ Prepared by the Sol-gel Method. Volume 23, issue 4. (2007) 465-468.
[9] C.T. Kresge, et al., MCM-41: A model system for adsorption studies on mesoporous. Journal of Nature. 359, (1992), 710.
[10] Wei Wang et al., Synthesis and characterization of high nickel-containing mesoporous silica via a modified direct synthesis method. Journal of Non-Crystalline Solids 352 (2006), 2180–2186.