Sodium silicate as source of silica for synthesis of mesoporous SBA-15

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Abstract. Ordered mesoporous silica SBA-15 was prepared using hydrothermal synthesis using sodium silicate (Na₂SiO₃) as the silica source and amphiphilic block copolymer Pluronic P123 as the structure directing agent. The influence of the mass Na₂SiO₃, ripening duration, aging time and calcination temperature on the structural and mesoporous properties of silica was studied. X-ray diffraction (XRD), Fourier transform infrared (FTIR), Scanning electron microscopy (SEM) and the nitrogen adsorption desorption using Brunauer Emmett Teller (BET) are some instruments used to characterize the results of investigation. From XRD analysis, SBA-15 synthesized from sodium silicate yield 2D-hexagonal symmetry (p6mm). From FTIR analysis, functional group Si-O-Si symmetric stretching modes and asymmetric Si-O-Si stretching modes were present. The sample with the highest mass of Na₂SiO₃ and the shortest aging time exhibited the largest surface area and large pore size. The results also showed the morphological structure could be tuned during ripening stage.

Keywords: Mesoporous, SBA-15, sodium silicate, characterization

1. Introduction

Mesoporous materials are made up of inorganic metal oxides such as silica or alumina. Silica mesoporous materials are synthesized by applying the use of surfactant to form regularly aligned assemblies that act as a template for the metal oxide followed by the removal of the template. The surfactant being used is the amphiphilic block copolymers, poly (ethylene oxide) – poly (propylene oxide) – poly (ethylene oxide). Its properties such as its amphiphilic character, biodegradability, low-cost commercial availability and mesostructural ordering action make it desirable to be used for SBA-15 synthesis[1]. It can be made up of pores ranging from 2 to 50 nm in width[2] and disordered micropores that allows interconnection between mesopores. SBA-15 products were found to be more hydrothermally stable as it has thicker walls. Its high internal surface area typically in the range between 400 and 900 m²g⁻¹ makes SBA-15 very versatile. The physico-chemical properties of SBA-15 materials can be possible tuned by varying the synthesis parameters which includes the pH solutions, reactant, additives and solvents, aging temperature, stirring and aging durations and temperature.

SBA-15 has been used as support in catalytic reactions where the high surface area enables better dispersion of particles[3]. It has also been known that SBA-15 is used in environmental analytics for separation and adsorption, advances optics and many more uses[4]. Mesoporous materials are usually synthesized by using tetraethylorthosilicate (TEOS) as the silica source. However, high cost of complex TEOS processing motivates the development of alternative silica
source \[^5\]. In this study, sodium silicate (Na\(_2\)SiO\(_3\)) was investigated to synthesize mesoporous SBA-15. It was also conducted to determine the effects of different mass of Na\(_2\)SiO\(_3\), ripening duration, aging time and calcination temperature.

2. Methodology

2.1 Synthesis of SBA-15 samples

SBA-15 samples were synthesized using Pluronic P123 (non-ionic triblock copolymer, EO\(_{20}\)PO\(_{70}\)EO\(_{20}\)) as a surfactant and Na\(_2\)SiO\(_3\) as the silica source. 4.0 gram of Pluronic P123 was dissolved in 80 gram of 2 M hydrochloric acid and 20 gram of distilled water with constant stirring for 1 hour at 40°C until homogeneous. Then 8.0 gram of Na\(_2\)O\(_3\)Si is added to the solution drop wise with vigorous stirring at the same time and temperature.

2.2 The effect of amount of Na\(_2\)SiO\(_3\) and aging time experimental procedure

The samples are aged at 40°C for 24 hours. The aging time is varied at 3, 6 and 16 hours. The solution is then treated hydrothermally at 100°C for 4 hours. The final product derived was filtered, washed and dried at 40°C. The samples were then calcined in a furnace at 550°C for 5 hours to decompose triblock copolymer \[^6\].

2.3 The effect of ripening duration and calcination temperature experimental procedure

4 gram of sodium silicate was slowly added into Pluronic123 – HCl solution under stirring condition and continuously stirred at 40°C for different duration for ripening process. After different hours of ripening step is completed, the solution was then transferred to the oven for hydrothermal aging process at 100°C for 4 hours. After 4 hours, the precipitate formed was filtered and washed with distilled water. Filtered precipitates are then dried in oven at 100°C for 4 hours. Dried sample are then divided into two and calcined at 550°C and 750°C respectively in a furnace.

2.4 Characterization of SBA-15 samples

The SBA-15 samples crystalline structure is characterized using X-ray Diffraction (XRD) patterns using the Rigaku Diffractometer. The 2θ angular regions between 0 and 5° were done at a scan rate of 0.004°/min (40 kV, 40 mA).

Adsorption and desorption isotherms of N\(_2\) was measured of the SBA-15 samples at -196°C using Micromeritics ASAP 2020. From the isotherms the BET surface area, \(A_{\text{BET}}\) pore size, and micropore area, \(A_{\text{mic}}\). The mesoporous area, \(A_{\text{meso}}\) was calculated by subtracting the \(A_{\text{mic}}\) from \(A_{\text{BET}}\).

Fourier Transform Infrared (FTIR) analysis of the SBA-15 samples was carried out using Perkin Elmer Spectrum One. The Field Emission Scanning Electron Microscope (FESEM) was used to capture the images of SBA-15 sample. The electron microscopy images of SBA-15 were taken on Carl Zeiss Supra 40 VP at acceleration voltage of 5 kV and magnification of x5000 and x20000.

3. Results and discussion

3.1 Synthesis of SBA-15 from sodium silicate as silica source

Figure 1 shows the XRD analysis for SBA-15 synthesized from sodium silicate. For different amount Na\(_2\)SiO\(_3\) and aging time imposed on the synthesis process, it can be seen diffraction peaks at almost the same intensities were observed. The peaks range from 0.32-0.38°, 0.70-0.72° and 1.04-1.06°. All samples exhibit very intense diffraction peaks at 2θ=1.048-1.06° which are characteristic of ordered SBA mesoporous materials with a 2-D hexagonal symmetry (p6mm). The
XRD patterns show that the samples synthesized have pattern characteristics of hexagonal mesostructures.

![XRD pattern chart](image1)

Figure 1. XRD patterns of SBA-15 sample at different sodium silicate mass (S1) 8 g, (S2) 6 g, (S3) 10 g and at different aging time (S1) 24 hours, (S4) 3 hours, (S5) 16 hours and (S6) 6 hours.

![N2 adsorption-desorption chart](image2)

Figure 2. N\textsubscript{2} adsorption-desorption isotherms of SBA-15 sample at different sodium silicate mass (S1) 8 g, (S2) 6 g, (S3) 10 g and at different aging time (S1) 24 hours, (S4) 3 hours, (S5) 16 hours and (S6) 6 hours.

Nitrogen adsorption desorption of the samples using the Micromeritics ASAP 2020 enables the determination of the surface area of the samples and the pore distribution whether it is microporous, mesoporous or macroporous. Figure 2 is the N\textsubscript{2} adsorption desorption isotherm of the SBA-15 samples. All samples exhibit the same adsorption isotherm trend that is the Type IV isotherm. Type IV isotherms indicates that the samples are mesoporous. Mass of Na\textsubscript{2}O\textsubscript{3}Si in the synthesis of the SBA-15 samples S1, S2 and S3 yields 54, 26 and 140 m\textsuperscript{2}/g surface area. It can be inferred that the greater the mass of the sodium silicate used, the greater the surface area developed from the synthesis. Even though the surface area varies with each sample with different sodium silicate mass, all three isotherms correspond to Type IV mesoporous materials.
The FTIR adsorption data was collected using the Perkin Elmer Spectrum One FTIR spectrometer. Figure 3 displays the frequency band of samples S1 to S6 of SBA-15 synthesized by sodium silicate characterized using FTIR to identify the functional groups present in those samples. It can be observed that all the samples exhibit peaks of almost the same frequency. Each peak is characteristic of a specific functional group. The peaks ranging between 785 to 801 cm\(^{-1}\) are due to the Si-O-Si symmetric stretching modes. The peaks located between 1063.05 to 1077.49 cm\(^{-1}\) are apparent due to the asymmetric Si-O-Si stretching modes. The silica from the sodium silicate on the surface of the sample is evident from the frequency peaks detected.

### 3.2 The effect of amount Na\(_2\)O\(_3\)Si and aging time

For the variation of aging time, the mass of the sodium silicate used was the same for the samples, which are 8g. In the terms of the aging time as the synthesis parameters, the shorter the aging time the greater the BET surface area of the samples. The samples S4, S6, S5 and S1 arranged according to ascending aging time which is 3, 6, 16 and 24 hours respectively. The surface areas of the samples S4, S6, S5 and S1 are approximately 208, 204, 132 and 53 m\(^2\)/g respectively. It can be inferred that the longer the aging time, the surface area reduces. This may happen due to the degradation of pores and breakage of fiber segments formed due to prolonged aging time. The samples however still correspond to Type IV isotherms classifying it as mesoporous materials.

All samples exhibit small micropore area. The micropore area makes up approximately 9-35\% of the total surface area. The samples are made up mostly of mesopores. The SBA-15 samples prepared have low microporosity have higher thermal stability (Barrabino, 2011). The pore width of all samples is also characteristic of mesopores that is in the range of 2-50 nm.

### Table 1. Porous properties of SBA-15 samples with varying sodium silicate mass and aging time

| Parameter | \(a\) | \(b\) | \(c\) | Pore size, nm | Average pore width, nm |
|-----------|------|------|------|----------------|------------------------|
| \(l\) (g) | \(d\) | \(e\) | \(f\) | \(g\) | \(h\) | \(i\) |
| S1 | 8 | 53.995 | 5.276 | 0.043 | 3.150 | 3.2338 | 4.2402 | 4.4338 | 3.1507 | 3.2338 |
| S2 | 6 | 25.961 | 6.212 | 0.042 | 6.619 | 6.619 | 11.042 | 7.196 | 6.619 | 6.619 |
| S3 | 10 | 140.42 | 36.062 | 0.100 | 2.794 | 2.933 | 5.449 | 5.226 | 2.9944 | 2.9330 |
| S4 | 24 | 53.995 | 5.2760 | 0.043 | 3.151 | 3.234 | 4.2402 | 4.4338 | 3.1507 | 3.2338 |
| \(l\) (hr) | \(d\) | \(e\) | \(f\) | \(g\) | \(h\) | \(i\) |
| S5 | 3 | 208.23 | 36.616 | 0.124 | 2.376 | 2.3801 | 3.3615 | 3.2504 | 2.3756 | 2.3801 |
| S6 | 6 | 132.38 | 18.756 | 0.087 | 2.618 | 2.6384 | 3.4435 | 3.2855 | 2.6177 | 2.6385 |

- **a-** BET surface area, m\(^2\)/g
- **b-** Micropore area, m\(^2\)/g
3.3 The effect of ripening duration and calcination temperature

The ripening duration were varied at 2h, 6h 16h and 24h and the effect on sample characteristics were studied. All samples exhibited similar nitrogen adsorption/desorption isotherm pattern but different isotherm values. The N\textsubscript{2} adsorption/desorption isotherms of all samples indicate different duration of ripening could change the mesostructural characteristic of SBA-15. Figure 4 shows the N\textsubscript{2} adsorption/desorption isotherm of a sample synthesize at 2h, 6h, 16h, and 24h ripening duration and calcined at 550°C.

![Figure 4. Nitrogen adsorption/desorption isotherm of sample ripened for (a) 2h (b) 6h (c) 16h and (d) 24h, which calcined at 550 degree Celcius.](image)

The SEM image of the samples in Figure 5 shows that spherical like aggregates was formed. As the ripening period increased, the sizes of the aggregates also increased. The aggregates alignment was found to be better aligned as the period of ripening increased. The large aggregates was formed in favor of the ripening conditions was also reported by Benamor et al. The trend of structural and textural properties of SBA-15 synthesized is in agreement with investigation by Chareonpanich et al.
Figure 5. SEM images of SBA-15 ripened for (a) 2h (b) 16h (c) 24h and calcined at 550°C

Figure 6: Nitrogen adsorption/desorption isotherm of sample ripened for 2h calcined at 750°C.
Figure 6 shows the SBA-15 sample ripened for 2h and calcined at 750°C. The Nitrogen adsorption/desorption pattern of samples calcined at 750°C showed a much smaller value compared to samples calcined at 550°C. All the samples calcined for both temperature 550°C and 750°C exhibits the type H1 hysteresis loop.

The SEM images SBA-15 samples calcined at 750°C in Figure 7 shows a significant difference compared to SBA-15 samples calcined 550°C in Figure 5. The particles has smaller surface area and pore volume at 750°C than that of 550°C. However, the pore diameter of mesoporous structure of SBA-15 have higher value compare to pore diameter calcined at 550°C. Table 2 displays the value of surface area and total pore volume is higher for samples calcined at 550°C but the higher pore diameter value for samples calcined at 750°C. As reported by Sahu et al., the surface area and total pore volume of SBA-15 samples would reduce as the calcined temperature increased.

Figure 7: SEM images of SBA-15 samples ripened for (a) 2h (b) 16h (c) 24h and calcined at 750°C
Table 2: Structural and textural properties of ripened at 40°C for various ripening period and calcined at 550°C and 750°C.

| Sample | \( S_{\text{BET}} \,^a \) (m²/g) | \( V_p \,^b \) (cm³/g) | \( D_{\text{BJH}} \,^c \) (Å) |
|--------|-------------------------------|-----------------|-----------------|
| 2h 550 | 183.2982                      | 0.080441        | 31.286          |
| 6h 550 | 222.561                       | 0.091274        | 30.235          |
| 16h 550| 172.7141                      | 0.087265        | 32.86           |
| 24h 550| 332.8657                      | 0.147502        | 28.922          |
| 2h 750 | 5.1029                        | 0.00267         | 36.481          |
| 6h 750 | 1.3588                        | 0.002104        | 127.5           |
| 16h 750| 1.2392                        | 0.002221        | 370.504         |
| 24h 750| 3.0783                        | 0.004184        | 84.147          |

\(^a\) BET surface area  
\(^b\) Total pore volume deduced from nitrogen adsorbed  
\(^c\) Pore diameter determined by the BJH method from the nitrogen desorption branch

4. Conclusion

Mesoporous silica SBA-15 was successfully synthesized under acidic conditions using sodium silicate as the silica source. The characterization showed that the materials have large specific surface area and developed mesoporosity. The surface area however is smaller as compared to the standard characteristics of SBA-15, which is around 500-1000 m²/g. The synthesis parameters of concern were the mass of the sodium silicate and aging time. From the result, the conditions for the synthesis of SBA-15 using sodium silicate with the highest mass of sodium silicate and the shortest aging time which is 10g and 3 hours respectively. Modifications with the mass and time can result in greater surface area of the SBA-15 product. Ripening duration due to different period of stirring and different calcination temperature also affect the structural properties of SBA-15 synthesized from sodium silicate.

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