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Synthesis And Characterization Of Mesoporous Silica Used As Catalyst In Biodiesel Production

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Abstract: Synthesis and characterization of silica nanoparticles were investigated. Cetyltrimethylammoniumbromide (CTAB) was used as a templating agent for the preparation of mesoporous silica materials starting from sodium silicate solutions using a sol-gel method. Sodium silicate was used as the silica source. The morphology and size of silica nanoparticles was characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and transmission electron microscope (TEM). Amorphous silica nanoparticle was characterized by Wide Angle XRD. The SEM images of the silica nanoparticles are pherical like aggregates was formed. But these samples have pore structure by TEM image and the size of nanoparticles is above 200 nm and the pore size is in the range 2 to 50 nm. The synthesized silica nanoparticles were used as catalyst in Biodiesel production by tranesterification method. The yield percentage of biodiesel produced by using silica nanoparticles is higher than without silica nanoparticles.

Keywords: Mesoporous, sol-gel, biodiesel, tranesterification

1. Introduction

SiO_2 is ubiquitous in our environment; human exposure can occur from natural or anthropogenic sources. Advancement in nanotechnology in recent years has expanded the synthesis of nonporous silica nanoparticles (SiNPs) for many applications.[1] Silica particles with controllable porosity have recently attracted much attention due to their excellent optical, electrical and thermal properties and wide potential applications in catalysis, separations, microelectronics, drug-delivery systems, environmentally acceptable, structurally stable, chemically resistant to organic solvents and microbial attack and have high surface area and average pore size between 2–50 nm. Ordered mesoporous silica were first prepared by Yanagisawa et al.[2-3] Their large surface areas allow for binding at a great number of active sites distributed within the framework of these porous materials.[4] In addition, this system can facilitate the diffusion of gas molecules into pores in microporous systems [5], in which pore-diffusion limitations influence the adsorption equilibrium. A further benefit is often enhanced stability, under both storage and operational conditions, e.g. towards denaturation by heat or organic solvent. These are the reasons for intensive studies of immobilization of various enzymes onto mesoporous silica materials as supports [6 - 10]. Recently, major challenges for the preparation of nanoparticle systems include development of new compositions and the fabrication of multifunctional systems with specific architectures. Thus, numerous particle systems have been developed and fabricated by assembling diverse nanoparticles on, encapsulated within, or integrated both inside and on the surface of silica nanoparticles using different synthesis methods. Properly coated or surface-modified nanoparticles can offer a high potential for numerous applications, due to change of their interfacial characteristic and electrical, magnetic or optical properties [11]. Thus, extensive research has been devoted to the synthesis of core/shell particles. It is known that silica particles synthesized by the Stöber method [12] Mesoporous silica nanoparticles 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 [13]. In this study, sodium silicate (Na_2SiO_3) and SiO_2 were investigated to synthesize mesoporous silica nanoparticles. It was also conducted to determine the effects calcination temperature.

2. Research Material and Methods

2.1 Materials

CTAB (Cetyltrimethylammoniumbromide) were purchased from BDH. Sodium silicate, sodium hydroxide, orthophosphoric acid and other chemicals used in this investigation, were purchased from commercial market.

3.2 Synthesis of Mesoporous Silica Nanoparticles

By using sol-gel method, sodium silicate was used as silica source. Cetyltrimethyl ammoniumbromide (CTAB) was used as template. Sodium silicate was first mixed with distilled water to obtain an aqueous solution. CTAB was also dissolved in water to obtain a clear solution. The two solutions were then mixed stirred for 1 hr. The mixture had the molar composition of 1.0 Na_2 SiO_3: 0.25 CTAB: 180 H_2O. The pH value of the mixture was adjusted to pH 6.5 by adding Orthophosphoric acid. The mixture was heated in oven at 110˚C for 24 hr for crystallization. After the heating process, the solid was recovered by centrifuge. The solid was dried in oven overnight at 100˚C and then calcined in a

furnace at 550˚C for 6 hr to decompose CTAB and to obtain silica nanoparticles.

3.3 Characterization of Mesoporous Silica Nanoparticles

The samples crystalline structure is characterized using X-ray Diffraction (XRD) patterns using D8 ADVANCE Diffractometer, BRUKER. The Field Emission Scanning Electron Microscope (FESEM, Cross Beam Workstation) was used to capture the images of sample. The electron microscopy images of sample were taken on at acceleration voltage of 5 kV and magnification of 34.51KX .The morphologies of the synthesized nano silica were observed by transmission electron microscopy (FEI-Tecnai G2/ F30S-TWIN). Fourier Transform Infrared (FTIR) analysis of the samples was carried out using Perkin Elmer Spectrum spectrophotometer.

3.4 Preparation of Biodiesel from Waste Cooking Oil

In biodiesel production, waste cooking oil, sodium hydroxide and methanol were used. Silicon dioxide and silica nanoparticles were used as catalyst. First is the filtration of used oil and heating at 100˚C. Alcohol was mixed in the molar ratio of alcohol/ oil 1:3. 0.1% Silica nanoparticles and 0.1% SiO_2 was added respectively. 0.45% NaOH was also added and stirred at 60 ˚C about 2 hrs. The mixture was poured into the separating funnel and stood for overnight for the separation of biodiesel and glycerin. Then the biodiesel was washed by water at 60˚C about 6 times to clear completely. Finally dry the biodiesel at 100˚C in oven to remove moisture.

3.5 Measurement of Biodiesel Properties

The extracted biodiesel was analyzed by Fourier Transform Infrared (FTIR). The dynamic viscosity of the biodiesel was measured by U- tube at 40˚C. Kinematic viscosity was also calculated by using dynamic viscosity and density of the extracted biodiesel. The flash point was measured by SETA PM-93.

3. Result and Discussion

3.1 Synthesis and Characterization of Mesoporous silica

According to the XRD pattern, the silica nano samples are amorphous silica as shown in Figure (1).

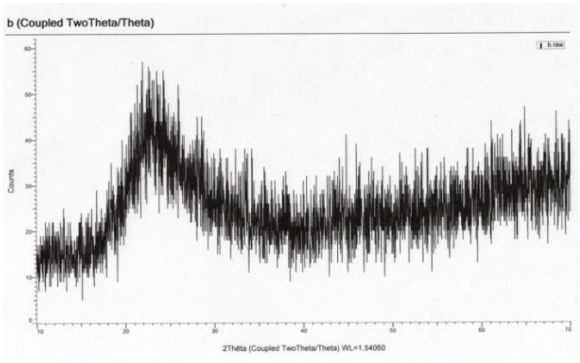

Figure 1: *XRD pattern of silica prepared*

The FTIR adsorption data was collected using the Perkin Elmer Spectrum Spectrometer. Figure 2 displays the frequency band of the sample synthesized by sodium silicate characterized using FTIR to identify the functional groups present in those samples. Each peak is characteristic of a specific functional group. The peaks ranging between 785 and 801 cm^{-1} are due to the Si-O-Si symmetric stretching modes. The peaks located between 1063.05 and 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.

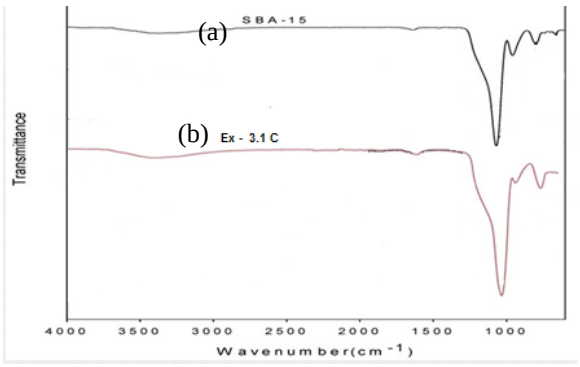

Figure 2: *FTIR of (a) SBA-15 and (b) Nanosilica prepared*

The SEM image of the silica nanoparticles shows that spherical like aggregates was formed. The sample was calcined for temperature 400°C, 500°C, 600°C, 700, 800°C. As silicates aggregate easily, the SEM images of the sample are not sharp and clear as shown in figure (3). Mesoporous structure of silica nanoparticles was also confirmed by TEM micrograph as it was shown in Figure (4). The samples have pore structure by TEM image and the size of nanoparticles is above 200 nm and the pore size is in the range 2 to 50 nm.

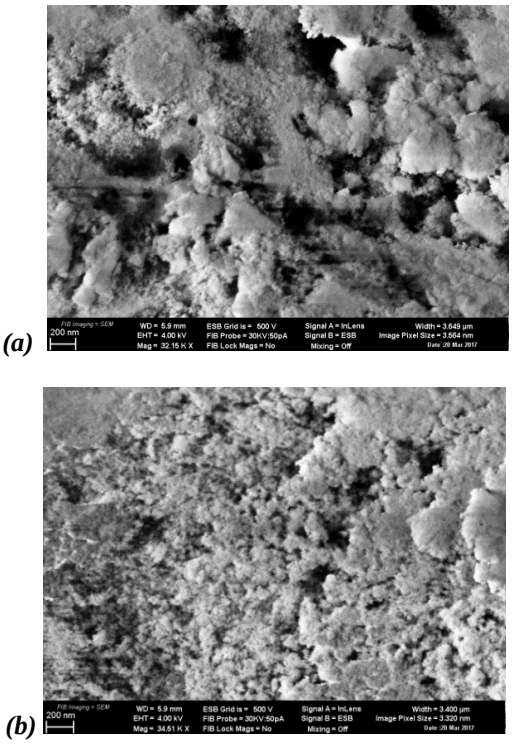

Figure 3: *SEM Images of Silica Prepared Calcined* at (a) 500°C and (b) 600°C

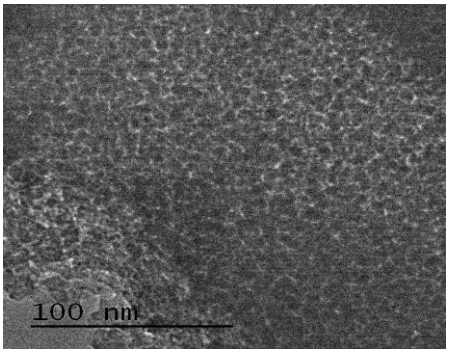

Figure 4: *TEM Images of Silica Prepared*

3.2 Preparation and Measurement of Biodiesel

The biodiesel by producing with silica nanoparticles was methyl linoleate according to FTIR result as shown in Figure (5). The yield percentage of biodiesel by using silica nanoparticles as catalyst was 95 % and it is higher than the percentage of biodiesel without silica nanoparticles (84%). The comparisons of the yield percentage of biodiesel are shown in table (1) and Figure (6). The properties of biodiesel with silica nanoparticles, commercial silica and without silica are shown in Table (2). These are within the standard range of biodiesel.

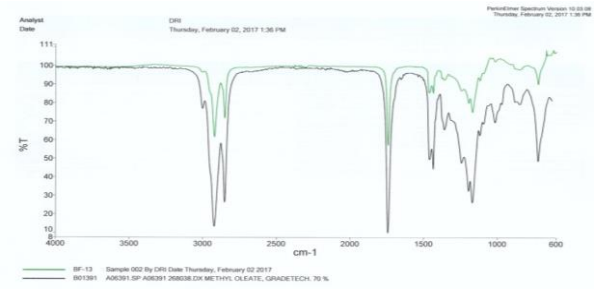

Figure 5: *FTIR of Biodiesel Prepared*

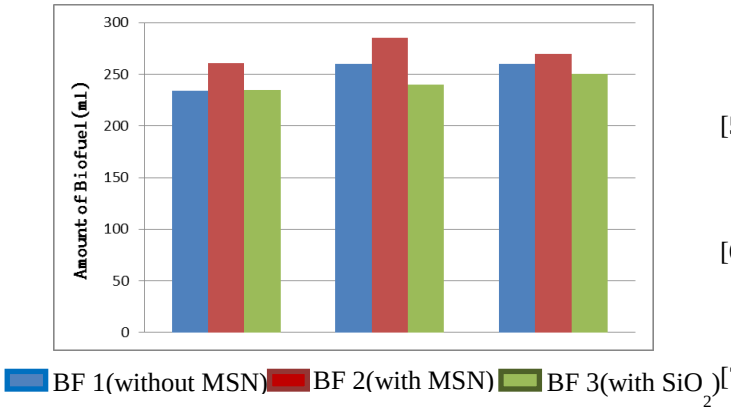

Figure 6: *Comparison of Yield Percentage of Biodiesel Prepared BF-1, BF-2 and BF-3*

4. Conclusions

Mesoporous silica was successfully synthesized under acidic conditions using sodium silicate as the silica source. The characterization showed that the materials are amorphous silica nanoparticles and shape is spherical like aggregates was formed. m2/g. The samples have pore structure by TEM image and the size of nanoparticles is above 200 nm and the pore size is in the range 2 to 50 nm. The catalytic activity toward transesterification of waste cooking oil with methanol and sodium hydroxide showed difference among the using commercial SiO_2 and without silica. The synthesized mesoporous silica showed the highest activity, with 95% yield of biodiesel at 60°C. The other two commercial SiO_2 and without silica yielded 78% and 80% biodiesel at the same condition. The properties of biodiesel prepared with mesoporous silica were within the standard reference range of Biodiesel.

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Author Profile

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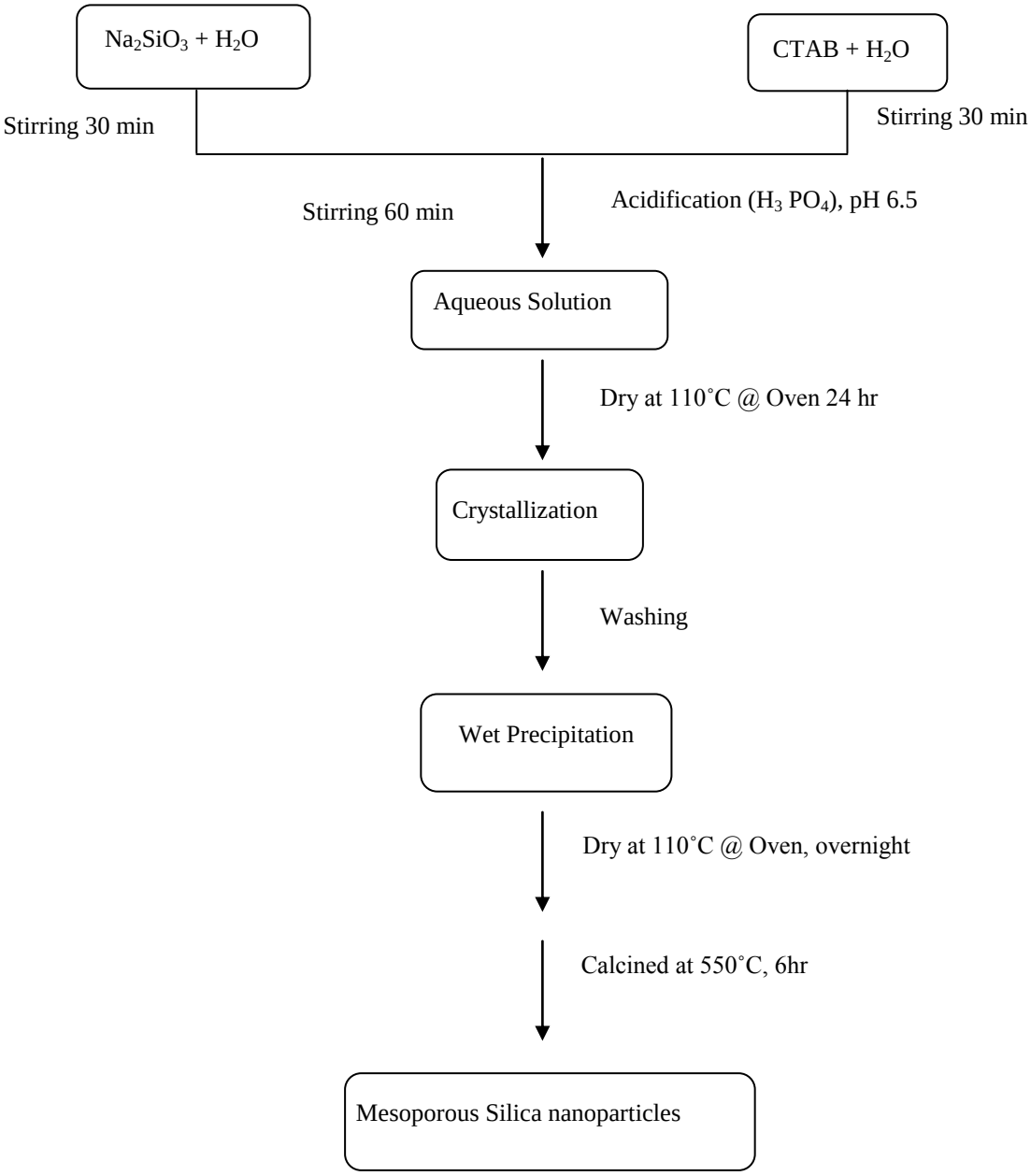

Flow Chart: *Preparation of Mesoporous silica nanoparticles*

Table 1: *Comparison of Yield Percentage of Biodiesel Prepared BF-1, BF-2 and BF-3*

Experiment		WCO (ml)	MeOH (ml)	BF(ml)	Average Yield (%)
BF-1 (without silica)	BF-1 A	300	100	234	78
	BF-1 B	300	100	260	86.7
	BF-1 C	300	100	260	86.7
BF- 2 (with synthesized silica)	BF- 2 A	300	100	261	87
	BF- 2 B	300	100	285	95
	BF- 2 C	300	100	270	90
BF – 3 (with commercial silica)	BF- 3 A	300	100	240	80
	BF- 3 B	300	100	235	78
	BF- 3 C	300	100	250	83

Table 2: *Properties of Biodiesel Prepared BF-1, BF-2 and BF-3*

No.	Experiments	Dynamic Viscosity (cP or mPa.S) (at 40˚C)	Kinematic Viscosity (mm^2 / s) (at 40˚C)	Density (g / m^3) (at 24˚C)	Flash Point (˚C)
1.	BF – 1 (Without SiO_2)	5.38	6.163	0.873	166
2.	BF –2 (With MSN)	5.21	5.947	0.876	166
3.	BF – 3 (With SiO_2)	4.73	5.412	0.874	162
4.	Standard	-	1.9 - 6	0.88	Above 160