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SEPARATION OF FATTY ACID BY FUNCTIONAL SBA-15, AG/SBA- 15 AND CHARACTERIZATION OF AG- NANOPARTICLE

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Abstracts

Rubber (*Hevea brasiliensis* L.) seed oil was collected and tested at the International joint research center , Southwest Forestry University in Kummin from Yunnan Province in China ,in 2017-2018. These oil extract fatty acid methyl ester (FAME) samples were separated the derivatives of fatty acid by using two catalytic reaction. The samples catalyst of Santa Barbara Amorphous -15 (SBA -15) and silver Santa Barbara Amorphous -15(Ag /SBA- 15) were characterized by X-ray diffraction (XRD), Scanning electron micrograph (SEM), transmission electron microscopy (TEM), N_2 adsorption – desorption isotherm for the characterization of Ag nanoparticle. Ag nanoparticle was found pore size and pore volume 8.628nm and 0.989755 cm^3/g. Moreover this FAME are mixed with SBA-15, Ag/SBA -15 catalysis were produced fatty acid derivatives. These mixing of fatty acid methyl ester (FAME) were conducted for characterization and identification by checking with FTIR and GC/Mass. Ten fatty acids was converted from the fatty acid methyl ester.

Keywords: Sample seed oil, Calcination, Nanoparticle of silver

Introduction

Many scientists prepared SBA-15 functionalized with $(CH_3O)_3$ $Si(CH2)_3$ $N(CH3)_3Cl$ (TPTAC) and further synthesized metal nanoparticles by anion exchange between grafted SBA-15 and metal precursors inside the channels as well as upon reduction of precursors. The amount of metal loading as well as the morphology of metal in host SBA-15 can be rationally controlled through repeating ion-exchange/reduction cycles in the TPTAC-SBA-15 silica host. Bui Thi Thanh ,*etal* (2012).

Mesoporous silica materials such as SBA-15 are preferred to be an ideal host for the deposition of metal nanoparticles as they possess a high surface area and pore volume, greater hydrothermal stability, and a hexagonal structure with tunable pore diameter (5–30 nm) with minimum hindrance, thus allowing easy diffusion of the reactants.

It is accepted that the unique architecture of SBA-15 can contain nanoparticles within mesopores with improved dispersal leading to the enhancement of their catalytic efficiency. Liu Yue, *etal*.(2017).

SBA-15 is a silica-based mesoporous material with uniform hexagonal channels ranging from 3 to 30 nm with a narrow pore size distribution. It is also one of the attractive supports with respect to high hydrothermal stability and larger surface areas, of 600–1000 m^2 g-1. Kim Na Young, *etal* .(2015). Huan Ma *etal*. (2016).

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Mesoporous silica SBA-15 having surface area (500-1500 m^2 g^{-1}), large pore size (50-100 Å) with narrow pore size distribution and thermal stability has been incorporated with sulfated zirconia on their surface to generate solid acid catalyst via direct synthesis or post synthesis route. It exhibited high activity for esterification reactions such as reaction of **fatty acid** with methanol for biodiesel. **Hermida** Lilis**, *etal*.(2010).**

Several patents have been granted for different types of adsorbents and techniques to separate fatty acids. Fatty acid methyl esters can be used as alternatives to fatty acids in the production of many oleochemicals (fatty alcohols, alkanol amides, a-sulfonated methyl esters, sucrose esters, and other fatty esters). Methyl esters are preferable to fatty acids as they yield higher purity finished products and require milder conditions during synthesis. Methyl esters are obtained by methanolysis of fats and oils in the presence of an alkaline catalyst, usually sodium methoxide, or splitting the fat by energy- and capital-intensive Colgate–Emery process followed by esterification of the resulting fatty acids with methanol, Udaya,*etal*.(2005).

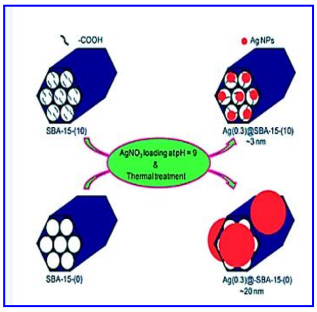
The catalyst of various amount ranged from 3 to 7 wt% was dispersed in methanol at temperature ranged from 50 to 70°C for a period of time prior to contact with the preheated feed-stock, providing a robust transesterification catalyst system. Jolius Gimbun ,(2012).

The use of these homogenous catalysts reduces the reaction temperature and controls product selectivity .However, they are associated with problems such as their sensitivity to free **fatty acids** and water present in the oil feedstocks and alcohol. The formation of soap resulting from reaction between free **fatty acids** and basic catalysts complicates the glycerol separation process thereby significantly affecting the yield of methyl esters. The employment of a heterogeneous catalytic system involving an environment friendly solid support can answer the problems arising due to the use of homogenous catalysts. The advantages of heterogeneous catalytic system include ease of regeneration, recycling of catalyst, ease in handling and scale-up. **Narayanan** Guru Krupa **,*etal*. (2012).**

Researcher obtained fine sized Ag particles whose size distribution was between 15 and 36 nm by polyol reduction. Silver powder of modified surfaces with controlled morphology can be prepared by several methods including the reduction of silver nitrate by reducing agents. An easy synthetic route for silver nanoparticles by hydrazine hydrate as reducing agent. The nanoparticles were characterized by various techniques. The silver particles' size show that the nanoparticles size is 92± 30 nm. Rahmani Behrad Mosavar ,*etal*.(2016). Ethanol in the solution phases reduced silver ions into silver nanoparticles. The linoleic acid caps the silver nanoparticles along with the reduction process thereby stabilizes the nanoparticles. Sliver nanoparticles having average diameter (size) of 12nm with the size range 7 – 15nm. The particles range in size from 8 to 50nm with mean diameter 24nm. Landage,*etal*.(2014).

The main aims and objectives of the study was to evaluate the performance of SBA-15 and Ag-SBA/15, to inform the mass production of catalysts for commercial sources to investigate the fatty acid derivatives from the FAME of selected rubber seed oil by using SBA-15and Ag/ SBA-15 catalysis reaction and to investigate the Ag- nanoparticle by the use of electronic spectroscopy.

The schematic illustration of the synthesis of Ag/ SBA 15catalysts showed by the Sadjadi .S and M.M.Heravi .(2017).



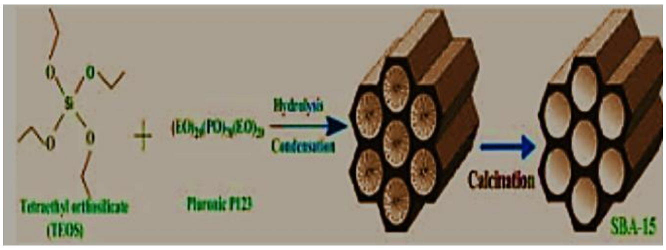
Materials and Methods

Rubber (*Hevea brasiliensis* L.) seed oil was collected at the International joint research center , Southwest Forestry University in Kummin from Yunnan province in China in 2017-2018.

Poly (ethylene glycol) ,propyleneglycol),(ethylene glycol),TEOS,$AgNO_3$, hydrazine hydrate,Potassium hydroxide, concentrated Sulphuric acid, Sodium carbonate (anhydrous), Hexane , Distilled water .Ethanol , Methanol ,Hydrochloric acid .

Preparation of SBA-15 and Ag/SBA -15Catalysts

According to the synthesis of mesoporous SBA- 15 figure showed by the literature survey Chaudhary Vasu And Sweta Sharma (2016).



The SBA catalysts were prepared as follows, 2 g of P123 was dissolved in 15 mL of distilled water at 40 °C, then 55 mL of 2 M hydrochloric acid was added slowly from the dripping funnel with vigorous agitation. The mixture was stirred for 3 h at 40 °C, then phosphotungstic acid (the loading amount of SBA was 10, 15, 20, 25, and 30%) was dissolved in water and added into the reaction. Subsequently TEOS was added slowly with vigorous stirring, resulting in a clear solution. The solution was transferred to a water-heated Teflon reactor and kept for 24 h at 100 °C, then filtered under vacuum and washed with deionized water and ethanol. After drying at 90 °C for 12 h, it was calcinated for 5 h at 550 °C in air, resulting inSBA ‑15 catalysts. (Min Li ,(2008), **Narayanan** Guru Krupa **,*etal*.,** Bui Thi Thanh Ha,*etal*..(2012)Young Kim Na ,(2015) , Huan Ma , Rahmani Behrad Mosavar etal,(2016), Liu Yue,*etal* (2017).

In a typical experiment, the SBA-15 (0.5 g) was added to a solution of $AgNO_3$(0.04 g) in water (5 mL) and stirred for 24 h at 50 ˚C. The mixture was filtrated and washed three times with 5 mL water, and then dried in vacuum. Afterward, the dried sample was stirred with 5 mL of 1 M hydrazine hydrate at 60 ˚C for 3 min. The mixture was then filtrated, washed three times with 10 mL water, and dried at 100 ˚C at 5 mins an ovan. Finally, a white gray powder (Ag/SBA-15) was obtained. Similarly steps of Liu Yue *etal.* (2017).

Production of Fatty Acid Methyl ester

The two step of hydrolysis first step -1.5% of concentration of sulphuric acid, 40% of water and rubber seed oil l ,100g were placed to the three neck of round bottom flask at water bath 95 ˚ C for ten hours , then using separation funnel ,until separately two layers. the upper layer collected to do the next step.The upper layer, 1% of concentrated sulphuric acid and 40% of water were added again for eight hours using similar step. Fatty acid methyl ester were obtained, which components of fatty acid derivatives.

Characterization techniques

FTIR, SEM, TEM, and XRD investigation of the SBA -15 and Ag/SBA -15 samples were carried out. The mixing of catalytic FAME were subjected to FTIR (Nicolet IS 50 FTIR spectrophotometer in the range 500 - 4000 Spectrometry). The FTIR spectrum was recorded between 4500-500 cm^{-1} using the KBr pellet mode. The FAME sample was also analyzed using GC-MS (GC- MS analyzer of GC⁻2010 plus, SHIMADZU.GC-MS analysis were performed on a HP3050 gas chromatograph equipped).

The morphology of the SBA-15 and Ag /SBA-15 was characterized using field emission scanning electron microscopy (JSM 6701F, JEOL, Japan). transmission electron micrographs(TEM) were obtained using a field emission transmission electron microscope (JEM 2100F, JEOL, Japan) after dispersing the sample on a copper grid. The crystalline phases of the catalyst were identified using SBA-15and Ag /SBA -15 mesoporous silica was characterized by a combination of physical techniques. X-ray diffraction (XRD) patterns were recorded using a SIMENS, XRD 5005 powder diffractometer system with CuKα_ radiation (Kα =1.54056 ˚A) with 0.2 step size and 1 s step time over the range 0 < 2 < 10 Cu-Kα radiation to record the XRD pattern. N_2 adsorption – desorption isotherm 77K were obtained ASAP 2020 equipment from micromatritic.BET (Brunauer,Emmett and Teller) specific surface area of the SBA-15 and Ag /SBA -15 was recorded using BET technique (ASAP 2020, Micromeritics, USA).

Results and Discussion

Characterization of the catalyst: The mesoporous SBA-15 and Ag /SBA 15catalyst was synthesized by using a modified thermal process and the catalyst was characterized by electron microscopy. Figure (5) shows the scanning and transmission electron micrographs of the SBA-15 and Ag /SBA- 15 which reveals the presence of highly ordered hexagonal pores with tubular morphology.

Infra-red spectral data

The FTIR spectra of the investigated SBA-15 and Ag/SBA -15 sample and mixing of FAME samples analysis of the synthesized have showed in Fig (1-2). The IR spectrum data was recording by using Nicolet IS 50 FTIR spectrophotometer in the range 500 - 4500 cm^{-1} with the FTIR spectrophotometer. The determination of FTIR spectrum was obtained from the following data. The main peaks and their assignment to functional groups of SBA-15 and Ag/ SBA-15, the rubber seed oil is given in Table (1-2). The results showed characteristic strong absorption bands at 3431.79, -OH stretching in alcohol, 2970 ,2998 cm^{-1}, -CH stretching for CH_3 group ,1742 cm^{-1} for the ester carbonyl (C=O) functional groups, 1624.19 for -C=O stretching for keto-enol system and at 1446$cm^{-1}$for a double bond, respectively. The functional groups present in rubber seed oil is similar to the literature of Seal Soma, (2012) and Yousif Emad (2013).

Table 1 FTIR spectral Data the catalyst of SBA-15 and Ag /SBA-15 functional Group assignments

No	Frequency (cm^{-1})	Functional group
1	3431.79	- OH stretching in alcohol
2	2898.57	-CH stretching for CH_3 group
3	1624.19	-C=O stretching for keto-enol system
4	1417.12	-C=C stretching
5	1076.76	C-O stretching in alcohol
6	993.93	CH-bending (out of plane)
7	779.93	C -C bending (out of plane)

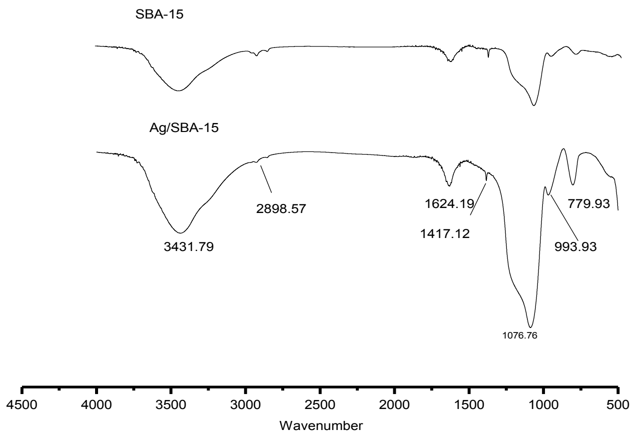


Figure 1 FTIR spectral Data of catalyst SBA-15 and Ag /SBA-15

Table 2 FTIR spectral Data the mixing of catalyst SBA-15 and Ag /SBA-15 fatty acid methyl ester functional Group assignments of Rubber seed oil.

No	Frequency (cm^{-1})	Functional group
1	3327.81	-OH stretching in alcohol
2	2898.57 - 2794.60	-CH stretching for CH_3 group
3	1728.27	- C = O stretching for acid system
4	1461.56	-C=C stretching
5	1121.29	C-O -C stretching (sym)
6	1017.21	C-O stretching in alcohol
7	718.73	C -C bending (out of plane)

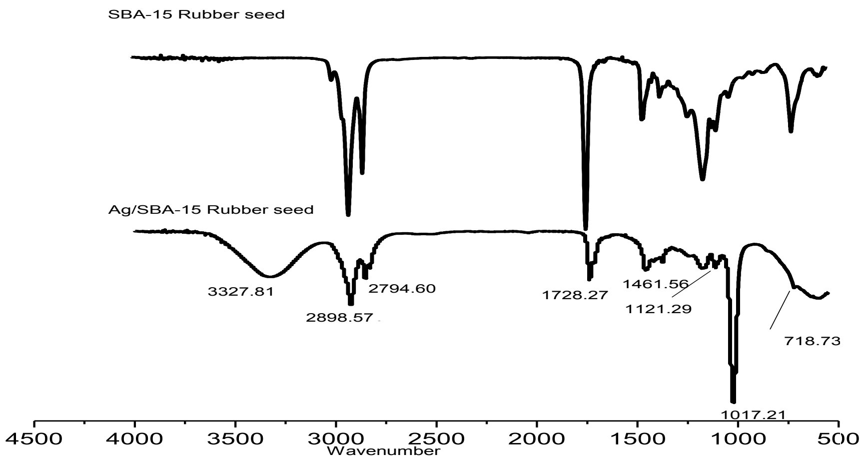


Figure 2 FTIR spectral Data of mixing FAME (Rubber seed oil) and catalyst SBA-15, Ag/SBA- 15

According to the GC/Mass data were shown in Table (3 to 4) Hexadecanoic acid, ethylester (16.48%),Linoleic acid ethyl ester (37.54%),(E)-9-Octadececanoic acid ethyl ester (35.45%) ,Octadecanoic acid ethyl ester (7.05%) by using catalyst of SBA-15. Hexadecanoic acid,ethyl ester (15.59%),Linoleic acid ethyl ester (36.11%) and (E)-9-Octadecenoic acid ,ethyl ester(34.94%),Octadecanoic acid ethyl ester were more yield percent than other fatty acids obtained by using Ag/SBA-15. FAME was showed separation effectively more activity by using two catalysts reaction.

Table 3 The derivatives of fatty acid from FAME (Rubber seed oil) by using catalystic of SBA -15.

No	Type of fatty acids	Retention time	Percentage %
1	Ethyl 9-hexadecenoate	37.618	1.39
2	Hexadecanoic acid, ethyl ester	37.964	16.48
3	Linoleic acid ethyl ester	39.223	0.31
4	9-Octadecenoic acid, methyl ester, (E)-	39.306	0.2
5	9,12-Octadecadienoic acid (Z,Z)-	39.74	0.49
6	Oleic Acid	39.826	0.95
7	Linoleic acid ethyl ester	40.073	37.54
8	(E)-9-Octadecenoic acid ethyl ester	40.155	35.45
9	Octadecanoic acid, ethyl ester	40.394	7.09
10	Cyclononasiloxane, octadecamethyl-	90.946	0.09

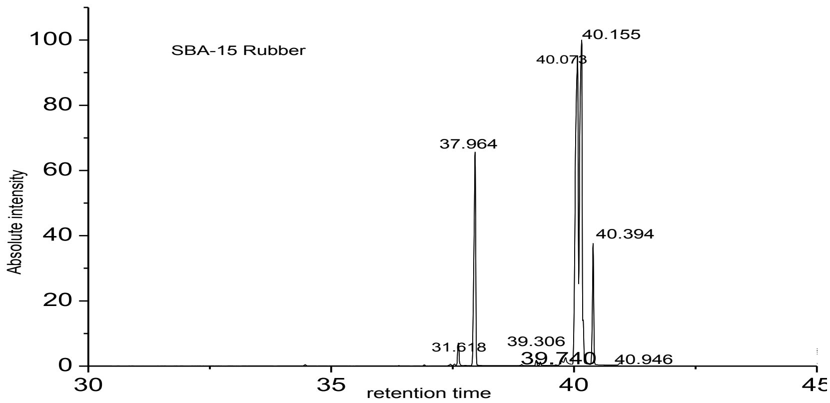


Figure 3 GC/Mass Data of mixing FAME (Rubber) and catalyst SBA-15

Table 4 The derivatives of fatty acid from FAME (Rubber seed oil) by using catalytic of Ag/SBA.

No	**Types of fatty acids**	**Retention time**	**Percentage(%)**
1	Ethyl 9-hexadecenoate	19.039	1.32
2	Hexadecanoic acid, ethyl ester	19.383	15.59
3	9,12-Octadecadienoic acid (Z,Z)-	21.514	0.75
4	Oleic Acid	21.629	0.93
5	Linoleic acid ethyl ester	21.989	36.11
6	(E)-9-Octadecenoic acid ethyl ester	22.109	34.94
No	Types of fatty acids	Retention time	Percentage(%)
7	Octadecanoic acid, ethyl ester	22.428	7.05
8	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	27.350	0.52
9	9,12-Octadecadienoic acid (Z,Z)-, 2,3-dihydroxypropyl ester	30.692	1.13
10	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	30.806	1.66

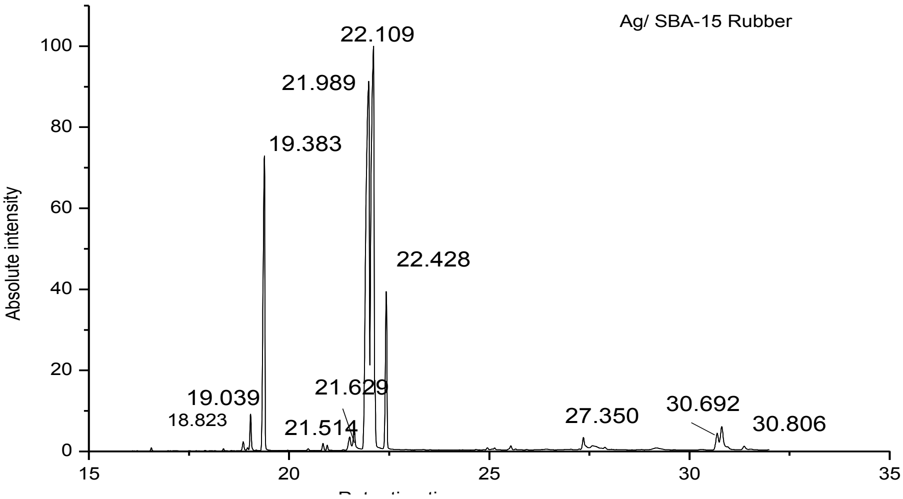


Figure 4 GC/Mass Data of mixing FAME (Rubber) and catalyst Ag/SBA-15.

The X- ray differentiation pattern of SBA- 15 and Ag/ SBA- 15 obtained from scheme of figure (5). the diffraction peak of Ag /SBA-15 was as like as the SBA-15. It is clear that the well-organized mesoporous structure of the support still remained after loaded with Ag. The defraction space d_{110} and d_{200} data were showed as table (5).

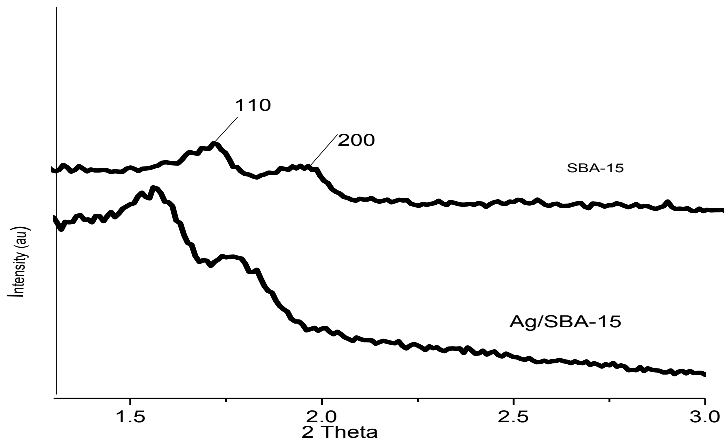


Figure 5 X- ray differentiation pattern of SBA- 15 and Ag/ SBA- 15

Table 5 XRD parameters of sample catalysts.

Sample	**d_{110}(nm)**	**d_{200} (nm)**	**Cell parameter (nm)**	
			d_{110}	d_{200}
SBA-15	5.13	4.53	7.25	9.06
Ag/SBA-15	5.56	4.93	7.91	9.86

The result from the SEM and TEM analysis data of SBA-15 and Ag / SBA -15 are showed in figure (5). The mesoporous structure of Ag/SBA-15were found at unifoundly distributed in the present inside or deposited on the outside of the channel of SBA-15.are agreed with those mentions by Rahamani (2016) and similarly research of Liu Yue (2017). Ag silver particles were found more than outside area because the pore size is a little large than SBA-15 pore channel.

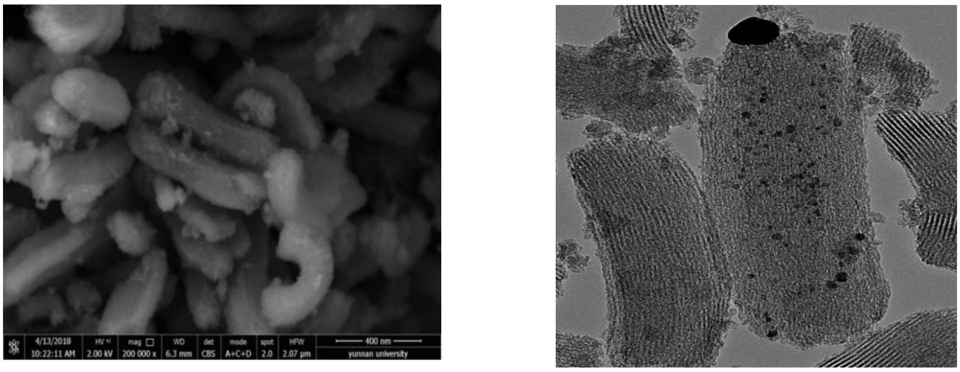


Figure 5 SEM image and TEM image of Ag/SBA-15

Table (6). BET-nitrogen absorption and desorption analysis about the surface area of SBA-15 (655 m^2/g) is larger than the surface area of the Ag /SBA -15, (461 m^2/g). The pore size of SBA-15 (6.5042 nm) and Ag/SBA-15 (8.6528 nm) and then the pore volume 0.923082 and 0.989774 m^2/g., Ag /SBA -15 surface area was small but pore size and pore volume were large. The average SBA-15 nanoparticle size 9.1468 nm and Ag -nanoparticle size 12.9871nm were obtained. The specific surface area, pore size, and pore volume decrease or increase with the dependent on the amount of silver content. Ag SBA/15 hexagonal shape mesoporous structure had shown to high separately total ester conversion rate and more adsorption and absorption rate.

Table 6 The result data of BET analysis of the SBA-15 and Ag/SBA-15

	SBA-15	**Ag/SBA-15**
Specific surface area,	655.9661m^2/g	461.9955m^2/g
Pore size	6.5042 nm	8.6528 nm
Pore volume	0.91468cm^3/g	0.989755cm^3/g
Porosity	90%	90%

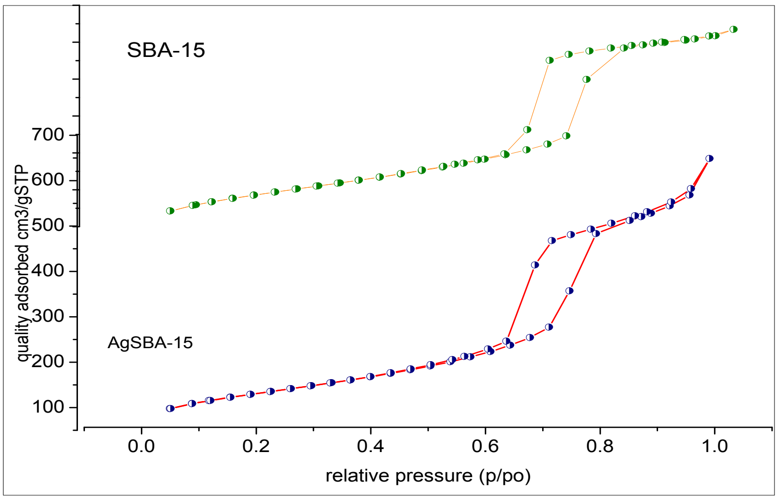


Figure 6 N_2 absorption and desorption isotherm of SBA-15 and Ag/SBA-15.

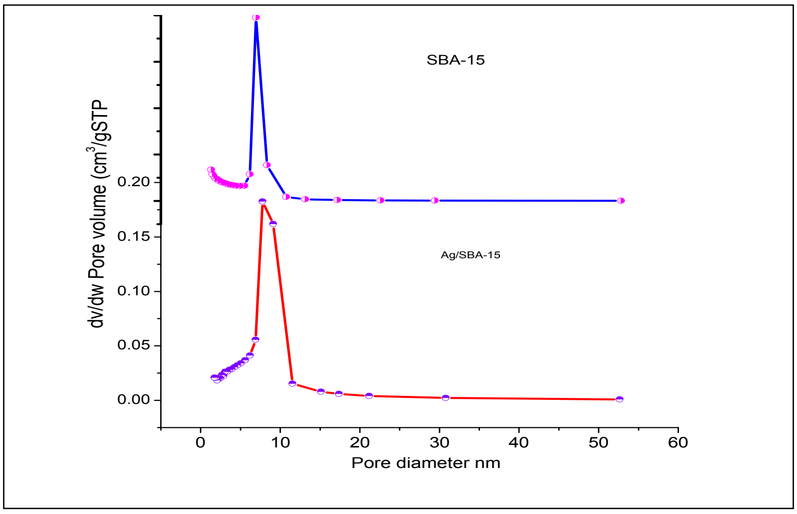


Figure 7 Barrett-Joyner- Halenda (BJH)Pore distribution curve of SBA-15 and Ag/SBA-15.

Conclusion

The derivatives of fatty acid were shown above data by using two catalytic reaction that it was obtained high yield percentage of fatty acids such as Oleic acid, linoleic acid etc. Ten fatty acids were successfully converted from the fatty acid methyl ester. And then silver nanoparticles confined outside of the channel of SBA-15 mesoporous channel like structure or deposits on the external surface of SBA-15. The meso porous structures were showed high surface areas, and tunable pore sizes of SBA-15 simplifies its used for sensor preparation and sensing application. Ag nanoparticles are one of the most attractive nanomaterials for commercialization uses. Silver nanoparticles are an important role of nanoscience and technology and nanomedicine. The large pore size supported the highest adsorptive quality and fastest kinetic activities.SBA-15 and Ag/SBA-15 were found to be an effective catalyst for the analysis of fatty acid from plants oil.

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