Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 10 (24): 3199-3206, 2010
ISSN 1812-5654

This article was presented in International Conference on Process Engineering and Advanced Materials 24th Symposium of Malaysian Chemical Engineers (15th-17th June, 2010)

Post Synthetically Functionalized SBA-15 with Organosulfonic Acid and Sulfated Zirconia for Esterification of Glycerol to Monoglyceride

Lilis Hermida, Ahmad Zuhairi Abdullah and Abdul Rahman Mohamed
School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pinang, Malaysia

Abstract: The pore structural properties and catalytic activity of SBA-15 post synthetically functionalized with organo sulfonic acid and with sulfated zirconia are presented. The SBA-15 incorporated with 3-(mercaptopropyl) trimethoxysilane (MPTMS) was prepared by post synthesis-grafting. Mild oxidation was carried out to obtain an acid catalyst (HSO_3SBA-15). Whilst SBA-15 immobilized with sulfated zirconia was prepared by reacting SBA-15 with solution of zirconiumoxychloride and urea at 90°C to ZrO_2-SBA-15. SZSBA-15 acid catalyst was obtained by sulfation of the ZrO_2-SBA-15 with H_2SO_4 solution at room temperature. The catalysts were characterized by surface area analysis, EDX, SEM, Fourier transform infrared (FTIR) spectroscopy and pulse chemisorptions of NH_3, followed by TPD of NH_3. The organo sulfonic acid functionalized SBA-15 catalysts (HSO_3SBA-15) were found to be more efficient solid acid catalysts for the esterification of glycerol with lauric acid to monolaurin at 160°C for 6 h using molar ratio of fatty acid to glycerol of 1:4. Excellent lauric acid conversion (94%) with high selectivity to monolaurin (70%) can be achieved using organo sulfonic acid functionalized SBA-15 catalyst with preparation condition of 20 h reflux time and MPTMS amount of 1 mL g^{-1} SBA-15.

Key words: SBA-15, post synthesis functionalization, organosulfonic acid, sulfated zirconia, glycerol, monoglyceride production

INTRODUCTION

Glycerol is a key co-product of biodiesel industry. Presently, rapid increase in biodiesel production is followed by an excess of glycerol generated. The oversupply of glycerol reduces its price. The low cost and the increase in glycerol availability make it attractive to exploit glycerol for synthesis of valuable products. For example, glycerol has been converted into high yield of 1,2-propanediol in the presence of Pt impregnated NaY zeolite as a catalyst and acrolein has been synthesized via dehydration of glycerol performed on a WO_3/ZrO_2 catalyst in a continuous flow fixed bed reactor (Ulgen and Hoelderich, 2009). Glycerol is also used for commercial production of monoglyceride through transesterification of glycerol with fat (triglyceride) or with Fatty Acid Methyl Ester (FAME) using homogeneous basic catalyst. Besides of that, monoglyceride is also produced industrially via esterification of glycerol with fatty acid.

Currently, direct esterification of glycerols with fatty acids for monoglyceride production relies on homogeneous catalysts typically strong mineral acids (Corma and Kumar, 1998; Formo, 1958). However, this technology creates large amounts of by- products and waste and utilizes high energy (Nakamura *et al*., 2008). Solid acid catalysts can offer advantages in the process design and may improve yield and selectivity to the desired product (Corma *et al*., 2005).

Acidic resins and zeolites have been used as solid acid catalyst for this application (Pouilloux *et al*., 1999; Aracil *et al*., 1992; Heykants *et al*., 1997). However, they were unfavorable for the monoglyceride production due to small pore diameter less than 8 Å, which makes them unsuitable for reactions involving the bulky molecule like fatty acid for monoglyceride formation (Perez-Pariente *et al*., 2003). On the other hand, MFI zeolite loaded with Pt was useful for fatty acid chemistry i.e., hydrogenating methyl elaidate (trans isomer) from an equimolar mixture with methyl oleate (cis isomer) as recently reported in the literature (Philippaerts *et al*., 2010). According to Wilson and Clark (2000), the effective solid acids having pore sizes between 20-100 Å were required for liquid phase reactions

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

Corresponding Author: Ahmad Zuhairi Abdullah, School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pinang, Malaysia

biodiesel (Chen *et al*., 2007), cyclohexanol with acetic acid (Garg *et al*., 2009) and acetic acid with n-butanol, as well as for transesterification of triacetin with methanol (Du *et al*., 2009). However, sulfated zirconia functionalized SBA-15 catalyst for the direct esterification of glycerols with fatty acids to monoglyceride has not been reported so far.

Moreover, mesoporous silicas of MCM-41 and HMS functionalized with organosulfonic acid were found to be excellent catalysts for formation of bisfurylalkanes and polyol esters (Van Rhijn *et al*., 1998). Meanwhile, SBA-15 functionalized with organosulfonic acid via direct synthesis route, followed by an oxidation step to create HSO_3SBA-15 catalyst has also been studied. The HSO_3SBA-15 catalyst was applied for esterification of fatty acid with glycerol (Diaz *et al*., 2001). It was found that the catalyst gave 50 and 57% selectivity to monoglyceride in the esterification at 120°C for 24 h reaction. Furthermore, in the esterification at 150°C for 6 h, the HSO_3SBA-15 catalyst gave 93% fatty acid conversion but lower selectivity to monoglyceride (around 20%). The poor performance of the SBA-15 catalysts was caused by the existence of organosulfonic acids in the high presence of structural micropores, so that the esterification would be slowed down. This finding is consistent with that reported by the other researchers (Huo *et al*., 1995; Zhou *et al*., 1998).

Post synthesis modification (grafting) that involves synthesizing SBA-15 silica materials before surface functionalization allows the synthesis of modified SBA-15 with highly ordered silica geometries even at moderately high organic loadings after the functionalization (Hoffmann *et al*., 2006; Garcia *et al*., 2007). Herein, we compared the pore structural properties between SBA-15 functionalized with organo sulfonic acid via post synthesis-grafting and SBA-15 incorporated with sulfated zirconia and we also studied their catalytic activity in esterification of glycerol with fatty acid at 160°C for 6 h reaction.

MATERIALS AND METHODS

Preparation of SBA-15: The SBA-15 materials used in this paper have been synthesized according to the method ascribed in literature (Zhao *et al*., 1998) with modifications. In a typical preparation, Pluronic P123 (4 g) was dissolved in water (30 mL) and 2 M HCl (120 mL) added at room temperature. The solution temperature was raised to 60°C. TEOS (8.50 g) was added to the solution upon a rapid stirring for 30 min and a precipitated product appeared. The stirring rate was then decreased and kept under this condition for further 20 h. The contents, then, were transferred to a polyethylene bottle and aged at 80°C for 48 h in an oven at static condition. After cooling to room temperature, the solid product was filtered, washed with deionized water and dried in air at room temperature for 12 h and at 100°C for 12 h. Calcination was carried out in static air at 300°C for 0.5 h and 550°C for 6 h to SBA-15.

Preparation of HSO_3SBA-15: Two gram of SBA-15 (evacuated at 120°C for 4 h) was dissolved in 50 mL of dry toluene under mild stirring. 3-(mercaptopropyltrimethoxy) silane (MPTMS) with varied amount (2, 6 and 10 mL) was added and the resulting mixture was refluxed for 20 h. The solid (-SH) was filtered, washed with acetone. The material was subjected to soxhlet extraction with ethanol for 24 h and then, dried in air. The -SH groups were converted to SO_3H groups by oxidation with 40 mL of 30 wt.% H_2O_2 solution with continuous stirring at 60°C for 24 h. The solid was filtered off, washed with water and ethanol, then acidified under reflux condition with 35 mL of 10% (w/w) H_2SO_4, followed by thorough washing with water, filtered off and dried at 333 K for 12 h. Hereafter, the synthesized catalysts will be denoted as HSO_3(1)SBA-15, HSO_3(3)SBA-15 and HSO_3(5)SBA-15 where values in the brackets represent MPTMS proportion (mL) per gram of SBA-15.

Preparation of SZSBA-15: SBA-15 functionalized with sulfated zirconia was synthesis as described previously (Garg *et al*., 2009). Four gram of SBA-15 (evacuated at 120°C for 4 h) was added to solution of 1.1622 g of Zirconium oxychloride ($ZrOCl_2.8H_2O$, Fisher product) and 1.083 g of urea in 120 mL of distilled water. The mixture was refluxed under stirring at 90°C for 5 h. The resultant product (ZrO_2SBA-15), was then filtered, washed with distilled water, dried at 100°C for 24 h and calcined in the air at 550°C for 6 h with a slow temperature increase of 1°C min^{-1}.

The obtained solid was subjected to sulfation with 1 (N) H_2SO_4 (15 mL g^{-1}) at room temperature for 3 h. The resultant solid was filtered, dried at 100°C and finally calcined in air at 550°C for 3 h with a slow temperature increase of 1°C min^{-1} to SBA-15 immobilized with sulfated zirconia (SZSBA-15).

Characterization techniques: The resulting catalysts were characterized by N_2 physorption using Quantachrome Autosorb-1 equipment for surface analysis, Transmission Electron Microscopy (TEM) using a Phillips CM 12, Scanning Electron Microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy using a Perkin-Elmer 2000 system and EDX in conjunction with SEM.

Characterization of acidity of the catalysts involved pulse chemisorption of ammonia, followed by a

Temperature Programmed Desorption (TPD) of ammonia using Micromeritics autochem II 2920 instrument. The sample was activated first by heating to 150°C in an inert helium environment for 2 h, then cooling to 127°C. The activation of the catalysts was followed by pulse chemisorptions of ammonia. During this step, 5 injections of ammonia were dosed onto the sample (to ensure the sample was saturated) by means of helium, flowing through a 5 cm^3 loop. Finally, a temperature-programmed desorption (TPD) of ammonia was carried out by increasing the temperature. At this step, the TCD (thermal conductivity detector) began scanning for ammonia. Data of signal was collected during a temperature ramp from 127-427°C for HSO_3SBA-15 and from 127-527°C for SZSBA-15. To obtain quantitative data, the signal was calibrated by injecting a known volume of the gas to be detected. The peak area of the signal can be obtained using the AutoChem peak editing software.

Activity studies: The catalytic activity of HSO_3SBA-15 catalysts for direct esterification of glycerols with lauric acids was carried out in a two-necked flask reactor equipped with a stirrer, a thermometer and a tube connected with a vacuum pump. The desired working pressure was maintained by the vacuum pump. This system readily permitted the elimination of water without significant variation of reaction volume (Sanchez *et al*., 1997). The reactor was immersed in a constant temperature bath.

The reactants, lauric acid (0.026 mol), glycerol (0.105 mol) and catalyst (0.7 g), were added to the reactor. Before an experiment was started, the system was flushed with nitrogen. The reaction mixture was heated to 160°C, when the reduced pressure was reached (50.8 cm Hg). Stirring was started and the reactants were stirred for 6 h.

Gas chromatography analysis: Mono-, di- and triglycerides were analyzed by gas chromatography using a Hewlett Packard 5890AII with a (15 m × 0.32 mm × 0.10 μm CP Sil 5CB) capillary column. The detector and injector temperatures were 380 and 250°C, respectively. The column temperature was set to 80°C for 1 min and was then programmed at 15°C min^{-1} to 330°C, which was maintained constant for 2 min. The sample of 100 μL was withdrawn from the reactor into a sample vial containing 100 μL water and 100 μL methyl acetate. The contents were vortexed and the organic phase was separated by means of centrifugation. Twenty milliliter organic phase was dissolved in 480 μL aceton and 100 μL of 0.2 M pentadecanoic acid as internal standard and then a direct injection was carried out into the gas chromatograph. The conversion was expressed with regard to the lauric acid transformation using the reaction coefficient for the formation of mono-, di- and triglycerides (Pouilloux *et al*., 1999), as shown in Eq. 1. In the same approach, the selectivity of mono-, di- and trilaurin was expressed by the ratio of the esters to all the various reaction products (corrected by the reaction coefficients) as seen in Eq. 2-4.

$$C\,(\%) = \frac{C_{Monoglyceride} + 2C_{Diglyceride} + 3C_{Triglyceride}}{C_{Monoglyceride} + 2C_{Diglyceride} + 3C_{Triglyceride} + C_{acid}} \times 100 \quad (1)$$

$$MS\,(\%) = \frac{C_{Monoglyceride}}{C_{Monoglyceride} \times 2C_{Diglyceride} \times 3C_{Triglyceride}} \times 100 \quad (2)$$

$$DS\,(\%) = \frac{2C_{Diglyceride}}{C_{Monoglyceride} \times 2C_{Diglyceride} \times 3C_{Triglyceride}} \times 100 \quad (3)$$

$$TS\,(\%) = \frac{3C_{Triglyceride}}{C_{Monoglyceride} \times 2C_{Diglyceride} \times 3C_{Triglyceride}} \times 100 \quad (4)$$

Where:

C = Lauric acid conversion (%)
MS = Monoglyceride selectivity (%)
DS = Diglyceride selectivity (%)
TS = Triglyceride selectivity (%)
C_{Acid} = Concentration of lauric acid (mol L^{-1})
$C_{Monoglyceride}$ = Concentration of monoglyceride (mol L^{-1})
$C_{Diglyceride}$ = Concentration of diglyceride (mol L^{-1})
$C_{Triglyceride}$ = Concentration of triglyceride (mol L^{-1})

RESULT AND DISCUSSION

Characterization of catalysts: The evidence for the presence of organosulfonic acid group in SBA-15 was confirmed by FT-IR spectra, as shown in Fig. 1. The

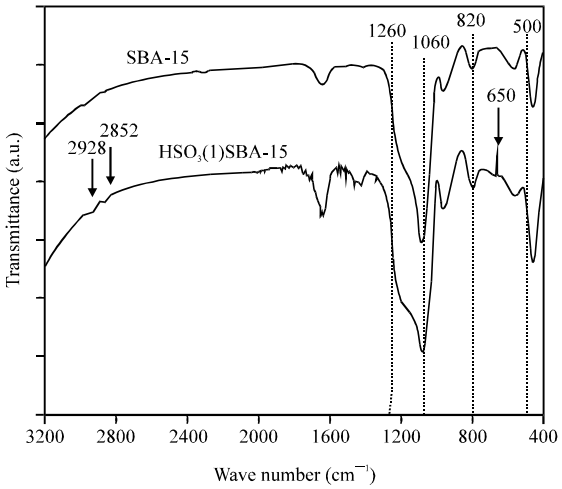

Fig. 1: FTIR spectra of SBA-15 and SBA-15 functionalized with organosulfonic acid

vibrations at 2928 and 2852 cm^{-1} are attributed to C-H stretching vibrations, while the band at 650 cm^{-1} relates to the C-SO_3H stretching vibrations. On the other hand, these peaks were absent in the parent SBA-15. FT-IR peaks at around 1060-1260, 850 and 500 cm^{-1} indicated Si-O-Si stretching vibration of the SBA-15 base materials. These observations are consistent with the literature (Saikia *et al*., 2007; Shon *et al*., 2007). Incorporation of sulfated zirconia in SBA-15 or SZSBA-15 was monitored by *in situ* EDX in conjunction with the SEM. According to the EDX analysis the SZSBA-15 contained Zr, as shown in Fig. 2.

The amount of acid sites of SBA-15 functionalized with propyl sulfonic acid via direct synthesis had been attempted by Zheng *et al*. (2005) using TPD ammonia performed in the temperature range from 50 to 527°C. They found that the SBA-15 functionalized with organo sulfonic acid catalysts showed two peaks of acid sites i.e., weak and medium acid sites in the NH_3-TPD curves related to the desorption of NH_3 on the region of 127- 427°C. At the higher temperature (427-527°C), the propylsulfonic group began to decompose. Whilst TPD of NH_3 for determining the acidity of sulfated zirconia functionalized SBA-15 has been performed in the region of 120-600°C by Chen *et al*. (2007), they found a peak mainly distributed on the region of 120-290 corresponding to weak acid sites and another peak at about 458°C indicating strong acid sites in the SZSBA-15 prepared by direct synthesis method.

In this study, the acid site concentrations of the SBA-15 post synthetically modified with propylsulfonic acid and sulfated zirconia determined by the pulse chemisorption of NH_3, followed by NH_3TPD in temperature region of 127-427°C for HSO_3SBA-15 and in temperature region of 127-527°C for SZSBA-15 are shown in Table 1. It was found that trend of the amount acid sites of SBA-15 silicas modified with organosulfonic acid decreased with the amount of MPTMS indicating that stacking fault was likely to increase with the quantity of MPTMS. The amount acid sites ranged between 24-42 μmol g^{-1}. While the catalyst of SBA-15 incorporated with sulfated zirconia having strong acid site has an acid site concentration of 37 μmol g^{-1}. NH_3-TPD profiles of HSO_3 (1)SBA-15 and SZ SBA-15, as shown in Fig. 3, showed peaks that are in agreement with those reported in the litareature (Zheng *et al*., 2005; Chen *et al*., 2007).

The textural properties of mesoporous silica of SBA-15 and SBA-15 functionalized either with different loadings of MPTMS or with sulfated zirconia are shown in Table 2. The average pore diameters of the modified samples are higher than the corresponding values for the

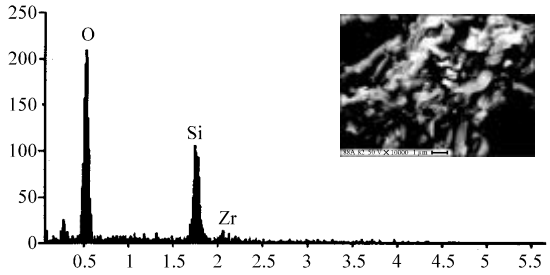

Fig. 2: EDX spectrum in combination with SEM of SBA-15 functionalized with sulfated zirconia (SZSBA-15)

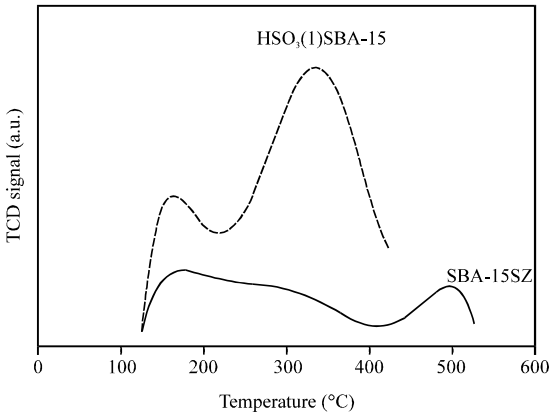

Fig. 3: NH_3 temperature-programmed desorption profiles of HSO_3(1)SBA-15 and SZSBA-15

Table 1: Acidic properties of the parent and modified SBA-15 materials

Silica materials	Acid site concentration[a] (μmol g^{-1})
SBA-15	-
HSO_3(1)SBA-15	42
HSO_3(3)SBA-15	24
HSO_3(5)SBA-15	27
SZSBA-15	37

[a]Determined from pulse chemisorption of NH_3, followed by NH_3 TPD

Table 2: Surface characteristic of the parent and modified SBA-15

Silica material	Total surface area[a]	Micro pore area[b] (m^2 g^{-1})	Meso pore area	Average diameter Å	Total pore volume (cc g^{-1})
SBA-15	542	149	393	59	0.795
HSO_3 (1)SBA-15	607	79	528	67	1.018
HSO_3(3)SBA-15	449	72	337	66	0.736
HSO_3(5)SBA-15	494	61	433	66	0.814
SZSBA-15	503	73	430	71	0.643

[a]Using the BET equation (S_{BET}), [b]Using the correlation of t-Harkins and Jura (t-plot method)

parent SBA-15. This observation was comparable to a previous publication (Rac *et al*., 2006) suggesting that the reaction conditions applied affect significantly the structure of SBA-15. The increase in the pore diameter after the functionalization via post synthesis method indicated that organosulfonic acid had indeed been located in the opening or outer surface of the mesoporous silica (Park and Prasetyanto, 2009) and that the sulfated zirconia is mainly incorporated into the wall of the silica rather than in the pores or the channels. It should be noted that besides relatively narrow pore distribution, the HSO_3 (1) SBA-15 had the highest total surface area, mesopore area and pore volume. This shows that the HSO_3 (1) SBA-15 has the most well defined structure as presented by pore size distribution curves in Fig. 4.

N_2 adsorption-desorption isotherms of the parent SBA-15 and the modified silica material are presented in Fig. 5. All of them exhibit type IV isotherms implying their ordered mesostructure with relatively narrow pore distribution. This result exposes that the mesoporous nature of the material is preserved even though the grafting had occurred. Although, the micropore volumes (Table 2) in all the modified silica materials were lower compared to that in the raw material, the structures were maintained.

TEM images of the parent and modified SBA-15 were presented in Fig. 6. All of TEM images i.e., parent SBA-15 (Fig. 6a), HSO_3(1)SBA-15 (Fig. 6b) and SZSBA-15 (Fig. 6c) showed the presence of well ordered mesoporous materials. SEM images of parent SBA-15, HSO_3(1)SBA-15 and SZSBA-15 presented in Fig. 6d, 6e and 6f, respectively, indicated as fibrous-type morphology of the parent and modified SBA-15 catalysts.

Activity of the modified SBA-15 catalysts: Esterification of glycerol with fatty acid to produce monoglyceride is a reversible reaction and stoichiometry of the esterification requires glycerol/fatty acid molar ratio of 1:1. In the present study, the glycerol esterification was carried out under the use of glycerol excess with the continuous removal of water from the reaction system. On the basis of this reaction condition, reaction steps for the glycerol esterification with fatty acid were irreversible parallel reactions to produce monoglyceride and by-product of diglyceride and triglyceride (Fig. 7), as reported in the literature (Sanchez *et al*., 1997).

The catalytic activity of the modified SBA-15 catalysts for esterification of glycerols and lauric acids to monolaurin in the solvent free condition at 160°C for 6 h is presented in Table 3. All the SBA-15 post synthetically modified with different amounts of organosulfonic acid (MPTMS) showed fatty acid conversion to be more than

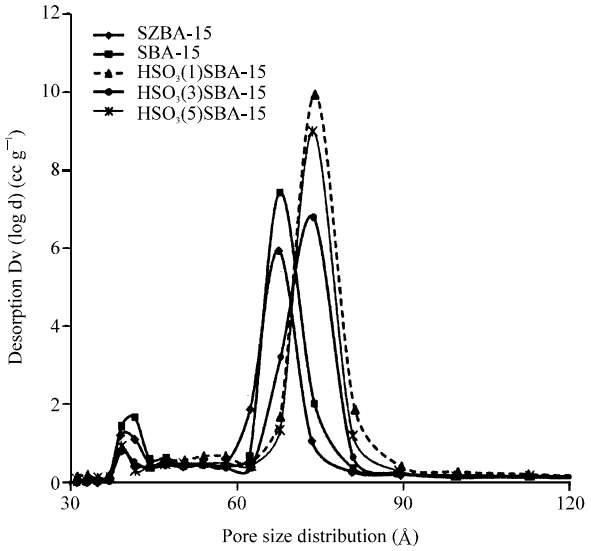

Fig. 4: Pore size distribution curve of the parent SBA-15 and modified SBA-15 catalysts

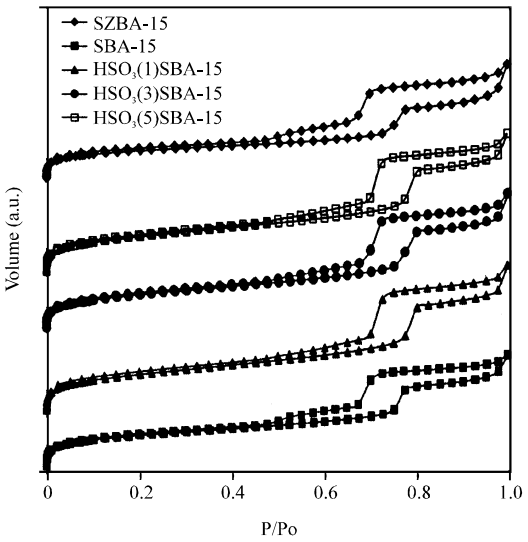

Fig. 5: N_2 adsorption-desorption isotherms of parent SBA-15 and modified SBA-15 catalysts

90%. The trend of selectivity to monolaurin was found to decrease with the amount of MPTMS used in the catalyst preparation and the highest selectivity to monolaurin that could be reached was 70% using HSO_3(1)SBA-15 with 94% fatty acid conversion. This can be explained by the higher mesopore surface area and the amount of site of the HSO_3(1)SBA-15 compared with the other organo sulfonic acid modified SBA-15 catalysts, as shown in Table 1 and 2. The amount of acid sites present and mesopore surface area in the organo sulfonic acid functionalized SBA-15 decreased in the order

Table 3: Activity of modified SBA-15 catalysts in esterificarion of glycerol with lauric acid

Catalysts	Acid site conc. (μmol g^{-1})	Fatty acid conv. (%)	Selec.to Mono-laurin (%)	Selec. to Di-laurin (%)	Selec. to Tri-laurin (%)
H SO_3 (1)SBA-15	42	94	70	30	0
H SO_3(3)SBA-15	23	93	53	43	4
H SO_3(5)SBA-15	27	96	57	43	0
SZSBA-15	36	62	68	32	0

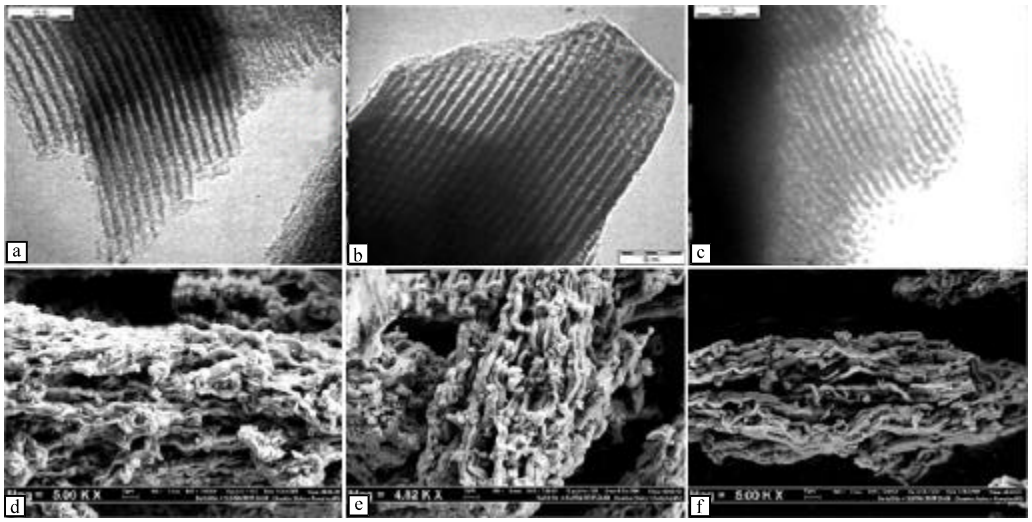

Fig. 6: TEM image of SBA-15: (a); HSO_3(1)SBA-15 (b); SZSBA-15: (c) and SEM image of SBA-15: (d); HSO_3(1) SBA-15: (e); SZSBA-15: (f)

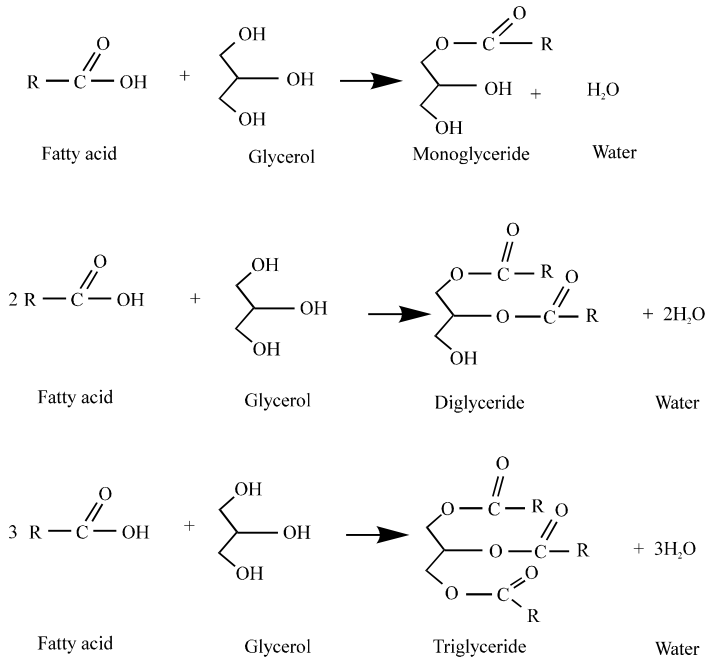

Fig. 7: Direct esterification of glycerols with fatty acid for monoglyceride and the formation of di-glyceride and tri-glyceride as by-product

HSO_3(1)SBA-15>HSO_3(5)SBA-15>HSO_3(3)SBA-15. Therefore, the selectivity to monolaurin also decreased in the similar order. In summary, catalytic activities of the solid acid catalysts were mainly influenced by both their active sites and surface area.

Although the amount of acid sites of HSO_3(1)SBA-15 was higher than that of SZSBA-15, HSO_3(1)SBA-15 had not strong acid sites like SZSBA-15. However activity of HSO_3(1)SBA-15 was much higher than the corresponding SBA-15 functionalized with sulfated zirconia (SZSBA-15). The SZSBA-15 gave 61% fatty acid conversion with 67% selectivity to monolaurin. Besides of the higher mesopore surface area of HSO_3(1)SBA-15 compared with SZSBA-15, this could be the consequence of its sufficient acidity for the esterification reaction.

Previously, it is reported that HSO_3HMS prepared by co-condensation for the esterification of glycerol with lauric for monolaurin gave about 80% fatty acid conversion and 52% selectivity at 112°C for 10.8 h (Bossaert *et al*., 1999). Moreover, HSO_3SBA-15 prepared by co-condensation used for the esterification of glycerol with oleic acid offered about 90% conversion and around 20% selectivity to monoglyceride at 150°C for 6 h reaction (Diaz *et al*., 2001). The fatty acid conversion and selectivity has been reported to be lower than the HSO_3(1)SBA-15 reported here.

CONCLUSION

We have shown that SBA-15 based solid acids prepared by post synthesis functionalized with varied proportions of organo sulfonic acid were efficient catalysts for esterification of fatty glycerol with lauric acid towards monoglyceride at 160°C for 6 h and gave more than 90% lauric acid conversion. The selectivity to monolaurin increased in the order HSO_3(3)SBA-15 < HSO_3(5)SBA-15< HSO_3(1)SBA-15 because the mesopore suface area of catalyst and the amount of acid sites follow the same order. The highest selectivity to monolaurin that could be reached here was 70% with 94% lauric acid conversion using HSO_3(1)SBA-15 catalyst.

Furthermore, the catalytic performance of HSO_3(1)SBA-15 was much better than that of SZSBA-15 in the same reaction. This could be due to the higher mesopore surface area and acid site concentration in the HSO_3(1)SBA-15 compared to those in the SZSBA-15. The SZSBA-15 gave 67% selectivity to monolaurin and 61% fatty acid conversion in the glycerol esterification.

ACKNOWLEDGMENTS

A Short Term grant with No.6035274 and Research University (RU) grants with No.814003; No.814004 from Universiti Sains Malaysia to support this work are gratefully acknowledged.

REFERENCES

Aracil, J., M. Martinez, N. Sanchez and A. Corma, 1992. Formation of a jojoba oil analog by esterification of oleic acid using zeolites as catalyst. Zeolites, 12: 233-236.

Bossaert, W.D., D.E. de Vos, W.M. van Rhijn, J. Bullen, P.J. Grobet and P.A. Jacobs, 1999. Mesoporous sulfonic acids as selective heterogeneous catalysts for the synthesis of monoglycerides. J. Catal., 182: 156-164.

Chen, X.R., Y.H. Ju and C.Y. Mou, 2007. Direct synthesis of mesoporous sulfated silica zirconia catalysts with high catalytic activity for biodiesel via esterification. J. Phys. Chem. C, 111: 18731-18737.

Corma, A. and D. Kumar, 1998. Possibilities of mesoporous materials in catalysis. Stud. Surf. Sci. Catal., 117: 201-222.

Corma, A., S.B.A. Hamid, S. Iborra and A. Velty, 2005. Lewis and Bronsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides. J. Catal., 234: 340-347.

Diaz, I., F. Mohino, E. Sastre and J. Perez-Pariente, 2001. 08-P-10-Synthesis and catalytic properties of SO_3H-mesoporous materials from gels containing non-ionic surfactants. Stud. Surf. Sci. Catal., 135: 285-285.

Du, Y., S. Liu, Y. Zhang, F. Nawaz, Y. Ji and F.S. Xiao, 2009. Urea-assisted synthesis of hydrothermally stable Zr-SBA-15 and catalytic properties over their sulfated samples. Micropor. Mesopor. Mater., 121: 185-193.

Formo, M.W., 1958. Ester reactions of fatty materials. J. Am. Oil Chem. Soc., 31: 548-559.

Garcia, N., E. Benito, J. Guzman, P. Tiemblo, V. Morales and R.A. Garciab, 2007. Functionalization of SBA-15 by an acid-catalyzed approach: A surface characterization study. Micropor. Mesopor. Mater., 106: 129-139.

Garg, S., K. Soni, G.M. Kumaran, R. Bal and K. Gora-Marek *et al*., 2009. Acidity and catalytic activities of sulfated zirconia inside SBA-15. Catal. Today, 141: 125-129.

Heykants, E., W.H. Verrelst, R.F. Parton and P.A. Jacobs, 1997. Shape-selective zeolite catalysed synthesis of monoglycerides by esterification of fatty acids with glycerol. Stud. Surf. Sci. Catal., 105: 1277-1284.

Hoffmann, F., M. Cornelius, J. Morell and M. Froba, 2006. Silica-based mesoporous organic–inorganic hybrid materials. Angew. Chem. Int. Ed. Engl., 45: 3216-3251.

Huo, Q., R. Leon, P.M. Petroff and G.D. Stucky, 1995. Mesostructure design with gemini surfactants: Supercage formation in a three-dimensional hexagonal array. Science, 268: 1324-1327.

Nakamura, R., K. Komura and Y. Sugi, 2008. The esterification of glycerine with lauric acid catalyzed by multi-valent metal salts. Selective formation of mono- and dilaurins. Catal. Commun., 9: 511-515.

Park, S.E. and E.A. Prasetyanto, 2009. Organocatalytic application of direct organo-functionalized mesoporous catalysts prepared by microwave. Top. Catal., 52: 91-100.

Perez-Pariente, J., I. Diaz, F. Mohino and E. Sastre, 2003. Selective synthesis of monoglycerides by using functionalised mesoporous catalysts. Applied Catal. A: Gen., 254: 173-188.

Philippaerts, A., S. Paulussen, S. Turner, O.I. Lebedev and G. van Tendeloo *et al*., 2010. Selectivity in sorption and hydrogenation of methyl oleate and elaidate on MFI zeolites. J. Catal., 270: 172-184.

Pouilloux, Y., S. Abro, C. Vanhove and J. Barrault, 1999. Reaction of glycerol with fatty acids in the presence of ion-exchange resins: Preparation of monoglycerides. J. Mol. Catal. A: Chem., 149: 243-254.

Rac, B., A. Molnar, P. Forgo, M. Mohai and I. Bertoti, 2006. A comparative study of solid sulfonic acid catalysts based on various ordered mesoporous silica materials. J. Mol. Catal. A: Chem., 244: 46-57.

Saikia, L., J.K. Satyarthi, D. Srinivas and P. Ratnasamy, 2007. Activation and reactivity of epoxides on solid acid catalysts. J. Catal., 252: 148-160.

Sanchez, N., M. Martinez and J. Aracil, 1997. Selective esterification of glycerine to 1-glycerol monooleate. 1. Kinetic modeling. Ind. Eng. Chem. Res., 36: 1524-1528.

Shon, J.K., X. Yuan, C.H. Ko, H.I. Lee and S.S. Thakur *et al*., 2007. Design of mesoporous solid acid catalysts with controlled acid strength. J. Ind. Eng. Chem., 13: 1201-1207.

Ulgen, A. and W. Hoelderich, 2009. Conversion of glycerol to acrolein in the presence of WO_3/ZrO_2 catalysts. Catal. Lett., 131: 122-128.

Van Rhijn, W., D. de Vos, W. Bossaert, J. Bullen, B. Wouters, P. Grobet and P. Jacobs, 1998. Sulfonic acid bearing mesoporous materials as catalysts in furan and polyol derivatization. Stud. Surf. Sci. Catal., 117: 183-190.

Wilson, K. and J.H. Clark, 2000. Solid acids and their use as environmentally friendly catalysts in organic synthesis. Pure Appl. Chem., 72: 1313-1319.

Zhao, D., Q. Huo, J. Feng, B.F. Chmelka and G.D. Stucky, 1998. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. J. Am. Chem. Soc., 120: 6024-6036.

Zheng, Y., X. Su, X. Zhang, W. Wei and Y. Sun, 2005. Functionalized mesoporous SBA-15 with propylsulfonic group as catalysts for esterification of salicylic acid with dimethyl carbonate. Stud. Surf. Sci. Catal., 156: 205-212.

Zhou, W., H.M.A. Hunter, P.A. Wright, Q. Ge and J.M. Thomas, 1998. Imaging the pore structure and polytypic intergrowths in mesoporous silica. J. Phys. Chem. B, 102: 6933-6936.