การเสื่อมสภาพของตัวเร่งปฏิกิริยาซัลโฟเนตเตดคาร์บอนบนพอลิเมอร์ในการสังเคราะห์ไบโอดีเซลที่อุณหภูมิสูง

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บทคัดย่อ

ไบโอดีเซลเป็นทางเลือกที่เป็นมิตรกับสิ่งแวดล้อมสำหรับน้ำมันดีเซลจากปิโตรเลียม ไบโอดีเซลผลิตได้จากปฏิกิริยาทรานเอสเทอริฟิเคชันของไตรกลีเซอไรด์กับแอลกอฮอล์ ตัวเร่งปฏิกิริยานับว่ามีบทบาทสำคัญในการผลิตไบโอดีเซล ซัลโฟเนตเตดคาร์บอนบนพอลิเมอร์ซึ่งสังเคราะห์ได้จากปฏิกิริยาซัลโฟเนชันของสารผสมคาร์บอนกับพอลิเมอร์ถูกใช้ในงานวิจัยนี้เพื่อศึกษาหาสาเหตุของการเสื่อมสภาพของตัวเร่งปฏิกิริยาวิวิธภัณฑ์ในปฏิกิริยาทรานเอสเทอริฟิเคชันของไตรกลีเซอไรด์กับแอลกอฮอล์ที่อุณหภูมิสูง และศึกษาผลจากขนาดแอลกอฮอล์และการใช้ตัวเร่งปฏิกิริยาซ้ำ รวมทั้งเปรียบเทียบผลที่ได้กับตัวเร่งปฏิกิริยาของแข็งอื่นๆ ที่สามารถหาซื้อได้ ซึ่งก็คือ ซัลเฟตเตดเซอโคเนียและแนฟิออน 50

จากผลของงานวิจัยพบว่าขนาดของแอลกอฮอล์มีผลต่อทั้งความว่องไวและการเสื่อมสภาพของตัวเร่งปฏิกิริยา เมทิลแอลกอฮอล์ให้ความว่องไวสูงสุดและการเสื่อมสภาพต่ำสุดเมื่อเปรียบเทียบกับเอทิลและบิวทิลแอลกอฮอล์ ตัวเร่งปฏิกิริยาซัลเฟตเตดเซอโคเนียให้ผลที่คล้ายกัน ความว่องไวของตัวเร่งปฏิกิริยาที่ลดลงเมื่อใช้แอลกอฮอล์ขนาดใหญ่สัมพันธ์กับการกีดขวางระหว่างอะตอมของสายโซ่หมู่อัลคิลขนาดใหญ่ เมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาอื่นๆ พบว่า ณ สภาวะของปฏิกิริยาเดียวกัน ซัลโฟเนตเตดคาร์บอนบนพอลิเมอร์มีความว่องไวกว่าซัลเฟตเตดเซอโคเนียและแนฟิออน 50 เนื่องจากมีความเข้มข้นของจุดกรดมากกว่า การเสื่อมสภาพของตัวเร่งปฏิกิริยาซัลโฟเนตเตดคาร์บอนบนพอลิเมอร์เกิดจากการหลุดออกของหมู่ฟังก์ชันซัลเฟอร์ลงในของผสมปฏิกิริยา ทำให้เกิดการเร่งปฏิกิริยาแบบเอกพันธุ์ ความสามารถในการชะเอาหมู่ฟังก์ชันซัลเฟอร์เพิ่มขึ้นกับขนาดของแอลกอฮอล์ กล่าวโดยสรุปคือ สำหรับการสังเคราะห์ไบโอดีเซลที่อุณหภูมิสูง ตัวเร่งปฏิกิริยาซัลโฟเนตเตดคาร์บอนบนพอลิเมอร์มีความว่องไวกว่าตัวเร่งปฏิกิริยาอีกสองชนิดที่มีขายในท้องตลาด และการใช้เมธานอลให้ความว่องไวสูงกว่า และตัวเร่งปฏิกิริยาเสื่อมสภาพช้ากว่าเมื่อใช้แอลกอฮอล์ขนาดใหญ่

คำสำคัญ : ไบโอดีเซล / ตัวเร่งปฏิกิริยาของแข็ง / ซัลโฟเนตคาร์บอนบนพอลิเมอร์ / การเสื่อมสภาพของตัวเร่งปฏิกิริยา

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The Deactivation of Sulfonated Carbon Catalyst Derived from D-glucose on Amberlite XAD1180 During The Biodiesel Synthesis at High Temperature

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Abstract

Biodiesel is an environmental friendly alternative for petrol-derived diesel. It can be produced from the transesterification reaction of triglycerides (TGs) with a low molecular weight alcohol using basic- or acidic- catalysts. Catalyst plays an important role on the production rate of biodiesel. Heterogeneous catalyst, namely, sulfonated carbon catalyst derived from D-glucose on Amberlite XAD1180 (P-C-SO_3H)-solid acid catalyst, was used in this research for studying the cause of catalyst deactivation at high temperature (120^oC) during the transesterification of triglycerides (TGs) with alcohol. Effects of alcohol size and catalyst re-using were investigated. Its activity was compared with those of sulfated zirconia catalyst (SZ) and Nafion 50, the commercially available catalysts.

From the results, size of alcohol had an effect on both the catalyst activity and deactivation. Methyl alcohol gave the highest activity and lowest deactivation compared to ethyl and n-butyl alcohols. Similar results were obtained for sulfated zirconia catalyst. Lower activity when using larger alcohol was related to the steric hindrance effect of the larger alkyl chains. In addition, P-C-SO_3H was found to have higher activity than the other two catalysts at the same reaction conditions due to its higher acid site concentration. The cause of catalyst deactivation was mainly from the leaching of sulfur functional group into the reaction mixture resulted in homogeneous catalytic transesterification reaction. The degree of leaching increased with alcohol size. In conclusion, for the transesterification of tricaprylin and alcohol at high temperature, P-C-SO_3H prepared in this work had higher activity compared to the commercial catalysts, and reaction with methanol gave better activity and lower catalyst deactivation.

Keywords : Biodiesel / Solid Acid Catalyst / Sulfonated Carbon Catalyst Derived from D-glucose on Amberlite Xad1180 / Catalyst Deactivation

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1. Introduction

Currently, biodiesel is an alternative for replacing petroleum diesel since it is more environmental friendly than the petrol-derived one. Biodiesel, mono-alkyl esters of free fatty acids, can be produced from the transesterification reaction of triglycerides (TGs) with a low molecular weight alcohol using basic- or acidic- catalysts [1].

Homogeneous catalysts, such as alkali hydroxides (NaOH, KOH), alkali alkoxides and alkali carbonates are now used for catalyzing the reaction of biodiesel synthesis with simple alcohols i.e., MeOH, EtOH, PrOH or BuOH. However, the use of these catalysts is limited by many problems, such as soap formation, loss of product activity, and increased difficulty in separating reaction mixture from the glycerol (a by-product) [2]. In addition, these catalysts cannot be recycled for re-utilization and are corrosive resulting in high production cost of biodiesel. The use of heterogeneous catalysts in biodiesel synthesis can decrease the production cost by simplifying the separation step, eliminating the corrosive problems of equipment in use and reducing cost of catalyst.

The cost of heterogeneous biodiesel production can be further reduced by using low grade feedstocks [3] and extending the catalyst life. Previous research [4] on biodiesel synthesis from poultry fat transesterification catalyzed by calcined hydrotalcite catalysts showed that catalyst deactivation occurred during the first reaction cycle, which decreased its activity significantly. Researches on other catalysts for biodiesel production also showed the significant catalyst deactivation when re-using in consecutive cycles even at low reaction temperature [5-8]. Therefore, this research focused on the stability of catalysts used for biodiesel synthesis at high temperatures (≥120°C). Sulfonated carbon catalyst derived from glucose on Amberlite XAD1180 (P-C-SO_3H), three simple alcohols (methyl alcohol, ethyl alcohol, and n-butyl alcohol) and tricaprylin ($C_{27}H_{50}O_6$) are used as the representatives for solid catalysts, alcohols, and free fatty acids, respectively. Commercial catalysts such as sulfated zirconia and Nafion NR 50 were also used for comparison purpose. The causes of deactivation were also investigated.

2. Experimental

2.1 Catalyst Preparation and Characterization

The main catalyst to be studied in this work is based on sulfonated carbon catalyst derived from glucose on Amberlite XAD1180 (P-C-SO_3H). The preparation of the catalyst is based on that given in Mo et al. [9]. This catalyst, P-C-SO_3H, was prepared by adding drop-wise of an aqueous glucose solution which consists of 1.2 g of D-glucose, 3 ml of deionized water, and 0.2 g of concentrated sulfuric acid into 2 g of pre-dried (100°C air) Amberlite XAD1180 until it was incipiently wet. The mixture was left at 100°C for 2 hours and 120°C overnight. After that, this mixture was pyrolyzed under dry N_2 at 300°C for 1 hour before it was sulfonated using concentrated sulfuric acid (1 g solid / 20 ml H_2SO_4) at 150-160°C for 13 hours under a dry N_2 atmosphere. The product was washed at least 7 times with hot distilled water until no sulfate ions were detected in the wash water and pH was the same as water. The resultant material is referred to as P-C-SO_3H in this study. For comparison purposes, commercially available catalysts namely sulfated zirconia (containing 1.73 wt. %S) provided by Magnesium Electron Inc. (MEI, Manchester, UK) and nafion NR 50 (with a swelled acid site concentration of 0.9 mequiv/g) purchased from Sigma-Aldrich were also used in some reaction studies.

The crystallinity of P-C-SO_3H was verified with a Scintag XDS 2000 θ/θ powder X-Ray Diffraction (XRD) at a wave length of 1.540562 Å and step size of 0.05°. A Nicolet Avatar 360 FTIR spectrometer equipped with a nitrogen-purged chamber and a DRIFT attachment was used for identifying types of chemical bonds on the catalyst surface. The total surface area and pore volume of the catalyst were derived from the amount of nitrogen adsorbed at -196°C using a Micromeritics ASAP 2020 BET apparatus. The catalyst was degassed for 3 hours at 120°C prior to the measurement. Thermalgravimetric analysis (TGA) was conducted using a TGA/SDTA 851 analyzer for measuring weight loss under a nitrogen flow rate of 50 ml/min and the temperature from room temperature to 1,000°C. Afterward, the total acid site concentration of the catalyst was measured using standard acid-base back titration. The solution of excess sodium hydroxide, 0.01N NaOH, was added to react with 0.05 g of dry catalyst at 100°C in air for at least 2 hours. After that the mixture was stirred for 20 hours in the shaker reactor at 250 rpm and 25°C. The liquid solution was then separated for titration with 0.02N HCl. Moreover, an elemental analysis (Galbraith Laboratory, Knoxville, TN) was performed for determining the sulfur content in the catalyst.

2.2 Reaction Studies

Transesterification reactions of triglyceride molecules (TGs) using tricaprylin (99.0 %, Sigma-Aldrich) with MeOH (99.8 wt. %, Sigma-Aldrich), EtOH (99.5 wt. %, Sigma-Aldrich), and n-BuOH (99.4 wt. %, Sigma-Aldrich) were conducted at high temperature (120°C) in a Parr 4590 reactor comprising of a stainless steel chamber, a glass liner, a three-blade impeller, and a thermocouple. In all experiments, a molar ratio of alcohol to triglyceride molecules (TGs) was 12:1 and catalyst loading was 10 % of the triglyceride weight. The reactor was pressurized with compressed nitrogen at 110 psi to keep the reaction mixture in the liquid phase. Typically, approximately 7.87 ml of tricaprylin was added into the reactor with corresponding amount of alcohol together with 0.787 g of solid catalyst. The mixture was heated to the desired temperature and continuously stirred. After reaching the reaction temperature, the reaction was started. The samples were collected at 30 minutes and/or 2 hours of reaction.

2.3 Analysis Methods

The analysis was started by drawing about 0.15 ml of sample from the reaction mixture via a microscale syringe with a pressure-lock button. After that, the sample was mixed with 0.8 ml of solvent (hexane: ethyl acetate = 1:1 v/v) at room temperature (25°C) and solid catalyst particle was separated out from the reaction sample by filter paper. Forty μl of residue homogeneous liquid was withdrawn and diluted with 5 ml of solvent using methyl laurate as an internal standard. Gas chromatography (GC) analysis was then performed. For GC analysis, a Hewlett-Packard 6890 gas chromatograph equipped with an automatic injector, an on-column inlet, a 15 m x 0.25 mm x 0.1 μm BPX5 column and an FID detector was used. At the injector, 1 μl of analyzed solution was injected to the column in which the temperature was initially held at 50°C for 1 min, then ramped up at 15°C/min to 270°C, and maintained there for 4 min. UHP helium was used as the carrier gas flowing at a constant rate of 12.7 ml/min.

3. Results and Discussion

3.1 Catalyst Characterization Results

After the preparation, the catalyst in this study, P-C-SO_3H was characterized by several methods. The BET surface area, total acid site density, and concentration of sulfonic groups of fresh P-C-SO_3H catalyst and sulfated zirconia catalyst are shown in Table 1. Characteristics of nafion NR 50 could be found in the work of López et al. [10].

BET surface area of fresh P-C-SO_3H catalyst given by BET apparatus was 197.52 m^2/g, which was higher than that of sulfated zirconia catalyst. Moreover, the sulfonic acid site density of fresh P-C-SO_3H catalyst reported by elemental analysis (assuming all sulfur atoms in the catalyst were in $-SO_3H$ form) was 2.83 mmolH+/g which was approximately 5 times higher than that of sulfated zirconia catalyst. The marginal acid density obtained from acid-base back titration over the sulfur elemental analysis was mainly due to phenolic-OH and −COOH groups on the catalyst. Most phenolic-OH and/or −COOH groups on fresh P-C-SO_3H catalyst were suggested to be associated with the carbon component formation from the pyrolysis/oxidation (under sulfonation conditions) of the glucose and/or carbon precursors, respectively [9].

Table 1 Characteristics of P-C-SO_3H and sulfated zirconia catalysts used in this study

Catalyst	BET surface area (m^2/g) [a]	Total acid density (mmol/g) [b]	SO_3H (mmol/g) [c]
Fresh SZ	155	0.37	0.54
Fresh P-C-SO_3H	197.52	5.54	2.83

[a] BET Surface area. Experimental error: ±1%;

[b] Acid-base back titration. Catalyst was reacted with excess 0.01N NaOH in aqueous solution at 25°C overnight before neutralizing with 0.02N HCl. Experimental error: ±6%;

[c] Based on sulfur elemental analysis. Experimental error: ±1%;

Fig. 1 shows the result of X-ray diffraction of fresh P-C-SO_3H catalyst. The result from X-ray diffraction of fresh P-C-SO_3H catalyst was similar to what previously reported by Mo et al. [9]. Fresh P-C-SO_3H catalyst exhibited quite identical XRD pattern with a broad peak centered around $2\theta = 25^o$ which was the characteristic of unordered carbon materials. From Fig. 2, the FTIR spectra of fresh P-C-SO_3H catalyst were discriminated by a broad band centered around 3,382 cm^{-1} and 2,931 cm^{-1} due to OH stretching and aliphatic C-H stretching, respectively, a band around 1,682−1,603 cm^{-1}due to C=O/S=O stretching, a band around 1,485−1,445 cm^{-1}due to aromatic ring stretching, and a band around 901−702 cm^{-1}due to aromatic CH wag. These peaks exhibited the important components in this catalyst.

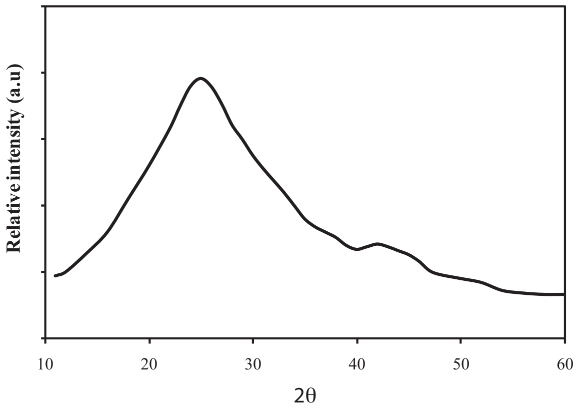

Fig. 1 X-ray diffraction pattern of fresh P-C-SO_3H catalyst.

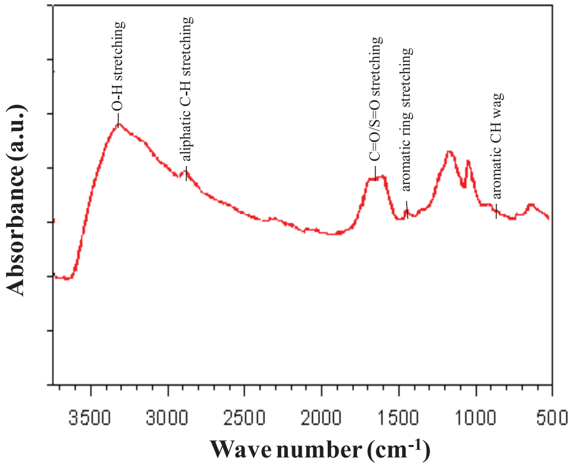

Fig. 2 FTIR spectra of the fresh P-C-SO_3H catalyst.

After that the P-C-SO_3H catalyst was heated in flowing nitrogen from room temperature to 1,000°C. The weight loss was investigated by using a Thermalgravimetric analysis (TGA) as shown in Fig. 3. Initial weight loss (solid line) below 150°C was due to water desorption. Sulfur (assumed to be in the form of $-SO_3H$) started to decompose at 150°C resulted in continuous weight loss until reaching steady state at around 650°C. This is supported by the derivative curve (dash line) which shows two significant peaks.

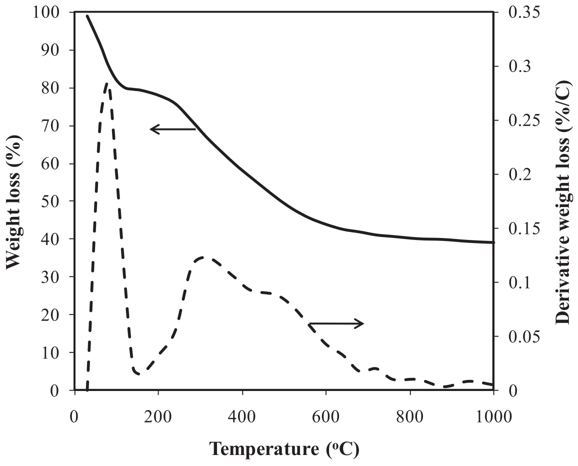

Fig. 3 Weight loss behavior of P-C-SO_3H catalyst characterized by the thermalgravimetric analysis (solid line) and its corresponding derivative curve (dash line)

3.2 Reaction Results

In this study, mass transfer limitation on the reaction rate could be eliminated and the measured rates were considered as kinetically controlled rates. The reaction conditions used in this study were similar to that used in the study by Chantrasa et al. [8] during the kinetics investigation of hydrotalcite catalyzed transesterification of tricaprylin. They had shown that catalyst particle size and stirring speed did not affect the reaction rate for the conditions in this study. Thus, the effects of alcohol size and catalyst re-using were then investigated.

3.2.1 Catalytic Activity and Re-using

To investigate the effect of alcohol size on the activity and stability of the catalyst during the transesterification reaction of TCP at 120°C, the catalytic activity in term of TCP conversion was measured when using MeOH, EtOH, and n-BuOH as the reactant. The TCP conversions obtained when using P-C-SO_3H catalyst are illustrated in Fig. 4. For the first reaction cycle using fresh catalyst, the highest activity with 64% TCP conversion was obtained when using MeOH, the smallest alcohol, while only 43% and 40% TCP conversions were obtained when using EtOH and n-BuOH, respectively. This implied that larger alkyl chains in larger size alcohols decreased the reaction rate which may be a result of the increased steric hindrance effect between alcohol and TCP. Used catalyst from the first cycle was then cautiously separated from the liquid mixture and reused in the second cycle and then the third cycle consequently.

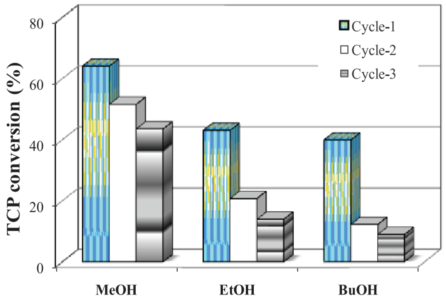

Fig. 4 The TCP conversion obtained at 30 minutes of reaction when using P-C-SO_3H catalyst for the transesterification reaction of TCP with methyl alcohol, ethyl alcohol, and n-butyl alcohol.

Considering the decrease in catalyst activity after re-using, the activity of P-C-SO_3H catalyst decreased significantly with reaction cycles, especially when it was used with large size alcohols. The TCP conversion obtained from the second reaction cycle of the transesterification reaction of TCP and EtOH or BuOH was less than a half of that from the first cycle. It was obvious that P-C-SO_3H catalyst was more stable when it was in the reaction mixture of TCP and MeOH than in the mixture of TCP and larger alcohols. Therefore, if there is a need to reuse this catalyst without any pretreatment, the transesterification reaction of TCP should be conducted with methanol.

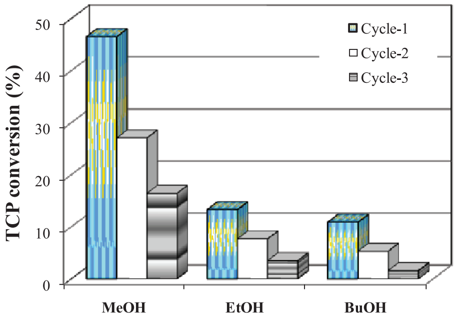

Fig. 5 The TCP conversion obtained at 30 minutes of reaction when using sulfated zirconia catalyst for the transesterification reaction of TCP with methyl alcohol, ethyl alcohol, and n-butyl alcohol.

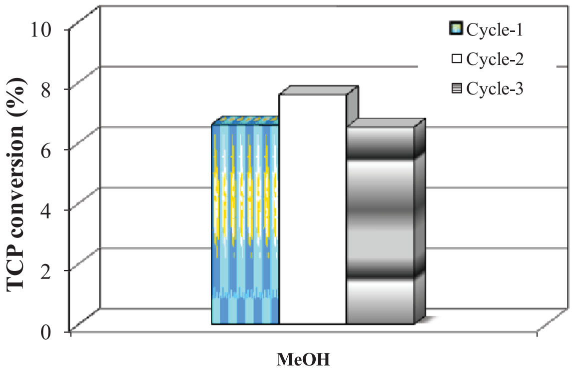

Fig. 6 The TCP conversion obtained at 30 minutes of reaction when using nafion NR50 catalyst for the transesterification reaction of TCP with methyl alcohol.

The activities of the commercially available catalysts such as sulfated zirconia and nafion NR 50, a polymer catalyst, were also measured as shown in Fig. 5 and 6. At the same reaction conditions, the activities of both catalysts are lower than that of the P-C-SO_3H catalyst prepared in this study. This could be due to the lower acid site concentration of these two catalysts (0.37 and 0.9 mmol/g for SZ catalyst and Nafion NR 50, respectively). The TCP conversion obtained when using sulfated zirconia decreased with reaction cycles and the size of alcohol molecules similar to the results from P-C-SO_3H catalyst. However, the decrease in TCP conversions with alcohol size and reaction cycle was much more obvious for sulfated zirconia catalyst. The deactivation of sulfated zirconia was also observed at lower reaction temperature during the transesterification of triacetin and methanol at 60^{o}C [7], the esterification of caprylic acid with ethanol at 75^{o}C [11], and the methanol-esterification of palmitic acid in sunflower oil at 60^{o}C [11]. For nafion NR 50, although, it has relatively low activity, it was quite stable at 30 minutes of reaction as can be observed from approximately the same TCP conversion for all three reaction cycles. This polymer resin was reported to exhibit the swelling behavior after contacting with reactants and expose more sites for reaction [7, 10]. Therefore, its activity tends to increase or stays constant when it is reused in consecutive cycles.

The decrease in catalytic activity of P-C-SO_3H catalyst was further investigated by conducting the experiment at longer reaction time. The results illustrated in Fig. 7 show that at 2 hours of reaction, the TCP conversions obtained from the transesterification reaction of TCP with methyl alcohol were approximately the same for all reaction cycles when using P-C-SO_3H catalyst. It indicated that although catalyst deactivation decreased the rate of reaction but a steady state can still be reached within 2 hours of reaction. However, for sulfated zirconia, the difference in TCP conversion after re-using can still be observed. It indicated that sulfated zirconia catalyst gave slower reaction rate, thus, more reaction time is needed for the reaction to reach steady state.

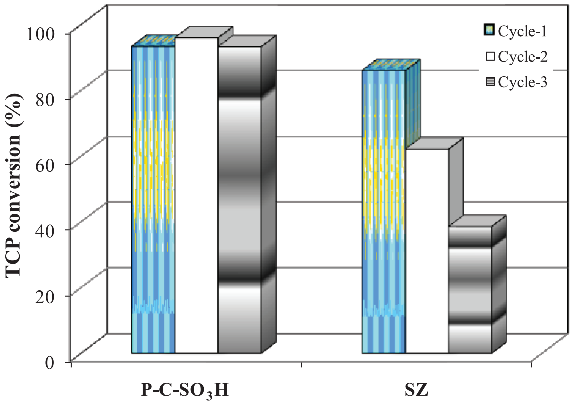

Fig. 7 The TCP conversion obtained at 2 hours of reaction when using P-C-SO_3H and sulfated zirconia catalysts for the transesterification reaction of TCP with methyl alcohol.

3.2.2 Catalyst Deactivation

The deactivation of sulfonated carbon catalyst has been investigated and reported by Mo et al. [5]. Polycyclic aromatic hydrocarbons were detected from the H-NMR spectrum of the reaction mixture after the esterification reaction of acetic acid and palmitic acid with methanol at 60°C. Thus, it was concluded that the deactivation of sulfonated carbon catalyst was substantially from the leaching of sulfonated polycyclic aromatic hydrocarbon into the reaction mixture [5]. In this study, the cause of deactivation at high temperature was further investigated by washing the P-C-SO_3H catalyst with methyl alcohol, ethyl alcohol, and n-butyl alcohol at 120°C for 30 minutes. The washed catalysts were then characterized by ICP method to determine their sulfur contents. As can be seen in Table 2, washing the catalyst in alcohols reduced the amount of sulfur content in the catalyst. Alcohols with larger alkyl chains can remove more sulfur from the catalyst surface. This could be caused by the hydrophobic characteristic of P-C-SO_3H catalyst. Ethyl and n-butyl alcohols, due to their large alkyl chains, have less polarity than methyl alcohol, thus, they could have a better contact with P-C-SO_3H catalyst and wash more sulfur out from the catalyst surface.

Table 2 The sulfur content of P-C-SO_3H catalysts after being washed in fresh alcohol at 120°C for 30 minutes

Catalyst	Sulfur content (%wt.) [a]	SO_3H (mmol-S)
Fresh P-C-SO_3H	9.05	2.83
Washed w/ MeOH	8.63	2.70
Washed w/ EtOH	8.28	2.59
Washed w/ n-BuOH	8.15	2.55

[a] Based on sulfur elemental analysis. Experimental error: ±1%;

Then the washed catalyst and the used alcohols after catalyst washing were used in the transesterification reaction of TCP with alcohols. The catalytic activity of the washed catalyst was measured after adding fresh alcohol and TCP and ramping the temperature to 120°C, the reaction temperature. In another experiment, TCP was added into the used alcohol after catalyst washing without additional catalyst, and the reaction was started when the temperature reached 120°C. The TCP conversions obtained from these two experiments at 30 minutes of reaction were compared with those from the previous experiments as shown in Fig. 8. If the deactivation occurred totally from the leaching of sulfonated polycyclic aromatic hydrocarbons by alcohols, the TCP conversion obtained when using the washed catalyst should be similar to that from the second cycle. However, the TCP conversion obtained when using the washed catalyst with methanol was lower than that obtained from the second cycle whereas the catalyst washed with ethanol and butanol gave approximately the same TCP conversions as those from the second cycle. This implied that, in case of methanol, with the presence of TCP in the reaction mixture, less sulfonated polycyclic aromatic hydrocarbons was leached out. It may be due to the hydroprobicity of TCP that covered the catalyst surface and prevented it from contacting with methanol, the highest polarity alcohol.

When the alcohol used in catalyst washing was used in the reaction without additional catalyst, it was found that the TCP conversion was as high as that from the first cycle. It suggested that what was leached out into the alcohol is the catalytic functional group for the transesterification reaction and homogeneous catalytic transesterification reaction occurred in this experiment.

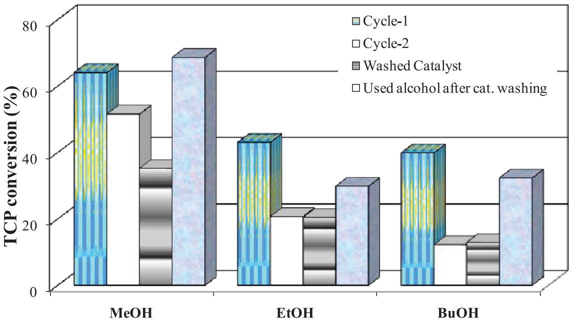

Fig. 8 Comparison of the TCP conversions at 30 minutes of reaction obtained from P-C-SO_3H catalyst, washed catalyst and alcohol used in catalyst washing for the transesterification reaction of TCP with methyl alcohol, ethyl alcohol, and n-butyl alcohol.

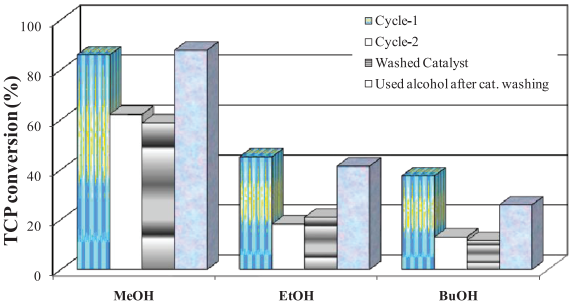

Fig. 9 Comparison of the TCP conversions at 2 hours of reaction obtained from sulfated zirconia catalyst, washed catalyst and alcohol used in catalyst washing for the transesterification reaction of TCP with methyl alcohol, ethyl alcohol, and n-butyl alcohol.

A similar experiment was performed on the sulfated zirconia catalyst except the TCP conversion was measured at 2 hours of reaction because sulfated zirconia gave a slower reaction rate compared to the P-C-SO_3H catalyst. The results were similar to those obtained when using P-C-SO_3H catalyst. Its catalytic activity decreased with reaction cycle and size of alcohol. Sulfur leaching was suspected to be the major cause of deactivation of this catalyst [11]. Due to the hydrophilic characteristics of the sulfated zirconia catalyst which is opposite to the P-C-SO_3H catalyst, more sulfur should be leached out when using methyl alcohol. This assumption was not proved in this study but it was in the work reported by Suwannakarn et al. [13]. The degree of leaching was reported to be depending on the alcohol size and contact time [13]. The activity of this catalyst was not easily regenerated [10] as being confirmed by an additional experiment in this study. The used SZ catalyst after the third cycle with ethyl alcohol was regenerated at 500°C in the stream of air and then used in the reaction. The TCP conversion obtained from this catalyst was less than 1% (data not shown) which was very small.

4. Conclusions

Activity of P-C-SO_3H catalyst was higher than those of the commercially available catalysts especially nafion NR 50, which is also the polymeric catalyst, probably due to its high acid density. Size of alcohol affected both the catalyst activity and stability. Methyl alcohol, with its smallest alkyl chain, when it was used in the transesterification gave the highest conversion. Lower catalyst activity when increasing alcohol size was suspected to be due to the steric hindrance effect from larger alkyl chain in the alcohol molecule. Catalyst deactivation was found when it was reused in consecutive reaction cycles without regeneration. It resulted in slower reaction rate especially when using larger size alcohol. Although the catalytic activity of P-C-SO_3H catalyst decreased with reaction cycles, the steady state can still be reached at less than 2 hours of reaction for the condition in this study. The cause of catalyst deactivation of both P-C-SO_3H and sulfated zirconia catalysts was mainly from the leaching of sulfur functional group into the reaction mixture. The degree of deactivation increased with alcohol size. In conclusion, for the transesterification of tricaprylin and alcohol at high temperature, P-C-SO_3H prepared in this work had higher activity compared to the commercial catalysts, and reaction with methanol gave better activity and lower catalyst deactivation.

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