

# Substantially Stabilized Superacid Incorporated SBA-15 with Calcium Bridging for Selective Esterification of Glycerol

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**Abstract.** The exploitation of the super acidity of heteropolyacids incorporated heterogeneous catalysts was only feasible if the heterogeneity of these catalysts was assured. To maintain the catalyst heterogeneity in polar medium, a novel two-step modification method was proposed to synthesize the highly active, yet stable heterogeneous catalyst, catered for selective esterification of monoglyceride. The surficial, structural and acidity properties of the modified catalysts were investigated via crucial characterization methods (N<sub>2</sub> BET, HRTEM, and FTIR). The collective evidences verified the predicted formation of calcium oxides (CaO) on the mesopores surfaces of the SBA-15 support after the first modification, and the successful subsequent 12-tungstophosphoric acid (HPW) functionalization. The superior stability of the synthesized catalysts (10wt%-HPW/CaSBA-15) was demonstrated (negligible change in both conversion – 75% and yield – 70%), without the need for catalyst regeneration. Such result was attributed to the strong interaction between HPW and SBA-15 via calcium bridging. Being alkaline in nature, calcium oxides in the inner pores readily reacted with highly acidic HPW introduced in the subsequent wetness incipient step, forming insoluble HPW acid sites on inner pore walls of SBA-15 via the calcium bridging. This modification deemed promising and other alkaline metals should be explored in the future.

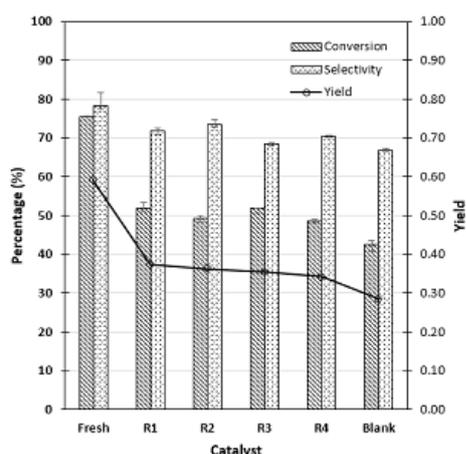
## 1. Introduction

In the past three years, the drastic collapse of Crude Oil Brent price from as high as USD 115 per barrel in June 2014 to only USD 48 per barrel in July 2017 [1]. With no sign of recovery, such abrupt price drop adversely impacted the development and production of biodiesel [2, 3]. Thus, converting glycerol, the major waste from biodiesel production to other value added products (glycerides, acrolein, citric acid, etc.) became popular to reduce its production cost [4, 5]. Yet, selective production of monoglyceride from glycerol is challenging without a highly selective catalytic system as diglyceride and triglyceride would be formed at the same time. Also, the unfavourable environmental impact and costly separation and purification procedures due to the use of homogeneous acid has pushed the research direction to highly reusable heterogeneous catalysts in industrial monoglyceride synthesis [6, 7].

In the effort of searching the suitable catalyst for selective esterification of glycerol with fatty acid, a particular group of high performance catalysts, mesoporous SBA-15 supported with Keggin



structured 12-tungstophosphoric acid (HPW,  $H_3PW_{12}O_{40}$ ) was of interest in this study [8-10]. A benign combination of high Brønsted acidity from HPW and size selectiveness of SBA-15 was anticipated to be the key factors for such highly selective esterification process. However, due to its polarity, the leaching problem of HPW from its support significantly lowered the catalyst reusability. In fact, its reusability was so low that it could only be used once before the catalytic performance was significantly deteriorated, as shown in figure 1.



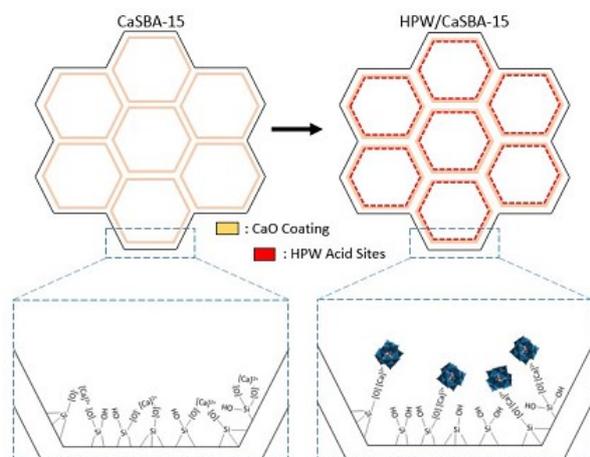
**Figure 1.** Conversion, Monolaurin Selectivity and Yield of the Fresh and Recycled HPW Incorporated SBA-15 in Esterification of Glycerol with Lauric Acid.

### 1.1. Reusability of HPW incorporated SBA-15

With reference to figure 1, along with many other available reports in the literature, the reusability, stability, and leaching study of HPW incorporated catalysts have become one of the most important and urgent matter to be addressed in order to continue exploiting the strong Brønsted acidity contributed by HPW [11, 12]. It was understood that only weak, physical interaction exists between the support and HPW acid sites [13]. The weak interaction resulted the vulnerability of these acid sites, causing these supported acid sites to be leached out into the reaction medium, ultimately contributed to the low reusability of the synthesized catalysts, or the need of catalysts regeneration [14]. Since then, researcher have proposed various solution to tackle such matter using different approach, including incorporation of insoluble HPW salts [15], “sandwiched” HPW method [10], or even on different supports [16-18].

### 1.2. A proposal to the matter of interest

Understanding the need for highly reusable yet performing heterogeneous catalyst in selective production of monoglyceride, this paper aims to improve the stability of the previously synthesized catalyst while retaining its already possessed superior catalytic performance. As far as the heteropolyacids are concerned, the super acidity is retained as long as the Keggin anion remains unchanged [19]. In this case, the conjugate base (the cation for the insoluble acid salt) must be chosen wisely in order to minimize the reduction of the acidity of the original acid which is in fact, responsible for the catalysis. As spontaneous reaction between alkaline and acidic component would produce the strong acid salt (hence the acid sites), it was hypothesized that by first modifying the mesopores surface within SBA-15 into mildly basic sites before functionalized it with HPW would yield a highly acidic yet stabilized heterogeneous catalyst with strong interaction between the support and acid. For such purpose, calcium, an element from the alkaline earth metals group (Group 2) was chosen due to its ability to form insoluble HPW salt ( $CaHPW_{12}O_{40}$ ) and its low toxicity compared to the rest of the elements from the same group. Such criteria was of importance as the catalysts would be applied in food related process (monoglyceride as emulsifiers). A simple yet informative schematic diagram which illustrates the idea of this proposal can be found in figure 2.



**Figure 2.** Proposed schematic diagram of the two-step calcium modified SBA-15 functionalized with HPW.

## 2. Material and methods

### 2.1. Synthesis of SBA-15

Initially, the typical SBA-15 was hydrothermally synthesized using Pluronic P123 as the organic template and tetraethyl orthosilicate (TEOS) as the silica source, as described in the established report by Zhao [20].

### 2.2. Calcium modification of SBA-15

SBA-15 was heated up to 378 K for 24 h to evacuate any possible moisture content. At room temperature, an appropriate amount of calcium nitrate tetrahydrate solution was added drop wise onto the SBA-15 as the calcium precursor via wetness incipient method with ethyl alcohol as solvent. To ensure the desired acid sites were formed, one to one molar ratio of calcium to HPW acid was followed. To synthesize CaSBA-15 for 10wt% HPW impregnation, 0.039 M of calcium nitrate solution was prepared. 1 ml solution per gram of SBA-15 was used based on the total pore volume of SBA-15 determined from BET analysis. The resulting sludge was slowly mixed (200 rpm) for 5 h. Then, the mixture was filtered, air-dried for 6 h followed by oven-dried at 353 K for 12 h. To convert the calcium precursors into basic calcium oxides, calcination of the powder was performed at a ramping rate of 2 K min<sup>-1</sup> to 823 K and stay for 3 h. The resulting white solid was labelled as “CaSBA-15”.

### 2.3. Functionalization of CaSBA-15 with HPW

The moisture of CaSBA-15 was evacuated using oven at 378 K for 24 h. Then, appropriate amount of HPW solution was introduced into CaSBA-15 via wetness incipient method using ethyl alcohol. The mixture was slowly stirred (200 rpm) for 5 h to allow acid-base reaction between HPW and surficial CaO on mesopores of the CaSBA-15. Then, the white powder was filtrated and dried at 298 K for 6 h followed by another 12 h in oven at 353 K. No calcination was followed to avoid disruption of characteristic SBA-15 p6mm hexagonal structure and the decomposition of HPW at high temperature [21]. The synthesized catalysts was labelled as “Xwt%-HPW/CaSBA-15”, with X as the weightage of HPW impregnated on CaSBA-15. The HPW needed was calculated using Equation (1).

$$X (\%) = \frac{\text{Weight of HPW}}{\text{Weight of HPW} + \text{Weight of CaSBA} - 15} \times 100\% \quad (1)$$

### 2.4. Material characterizations

The surficial, structural and chemical properties of the synthesized materials were investigated. By using Quanta-chrome Autosorb 1C automated gas sorption analyser, Nitrogen (N<sub>2</sub>) adsorption and

desorption on degassed synthesized materials (543 K, 6 h) enabled investigation on the type of materials, total surface areas, total pore volumes and the pore size distribution of the synthesized materials. Together with images analysis using TECNAI G2 20S-Twin high resolution transmission electron microscopy (HRTEM), the characteristic uniformed mesopores of pure, modified and functionalized SBA-15 could be verified. To verify key functional groups in pure, modified and functionalized SBA-15, the materials were subjected to Fourier Transformed Infrared (FTIR) analysis using KBr pellet method and IRPrestige-21 FTIR Spectrophotometer.

### 2.5. Catalyst performance and reusability tests

The developed catalysts were tested individually with selective monolaurin production from glycerol (99.8%) and lauric acid (99%). A temperature and pressure regulated batch reactor system made of magnetic stirring and heating mantle, a three-necked flask and a vacuum pump was used for such purpose. The catalytic performances of the HPW/CaSBA-15 catalysts were evaluated based on lauric acid conversion and monolaurin yield. The products sampled from specific reaction times were analysed using Agilent Technologies 7890A GC system equipped with CP-Sil 5CB (15 m x 0.32 mm x 0.1 mm) column. The lauric acid conversion and monolaurin selectivity were calculated as proposed by Pouilloux et al. [22]. The reusability test of the catalysts was accomplished by separating the used catalysts from the reaction mixture at the end of each runs. The whole reaction mixture was removed from reactor and centrifuged at high speed (4400 rpm, 5 mins). The liquid was removed from the vial and the remaining catalyst at the bottom of the vial was washed with acetone (99.8%) and deionized water to remove residual organic and polar compounds. The filtered, washed solid was oven-dried at 373 K for 24 h. The dried catalyst was then labelled R1 (R2 for second recycle) and reused in the same setup. The conversion and monolaurin yields were calculated.

## 3. Results and discussion

### 3.1. Surface analysis

From the Table 1, all catalysts exerted high specific total surface areas ranging from 564 to 766 m<sup>2</sup>g<sup>-1</sup>. Together with HRTEM structural analysis, the highly uniformed mesoporous SBA-15 was successfully synthesized and retained even after the two steps modification and functionalization. Further proof of such claim be seen in both nitrogen adsorption-desorption isotherms and the pore size distribution (PSD) of these materials in figure 3.

**Table 1.** Surface characteristics of SBA-15, CaSBA-15 and HPW/CaSBA-15.

Catalyst	Total Surface Area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	Mesopore Surface Area (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	Total Pore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>c</sup>	Mesopore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>d</sup>	Average Pore Size (Å) <sup>e</sup>
SBA-15	766	578	0.99	0.90	70
CaSBA-15	629	468	0.67	0.60	63
10wt%-HPW/ CaSBA-15	604	459	0.87	0.79	63
20wt%-HPW/ CaSBA-15	564	408	0.69	0.61	58

<sup>a,c</sup>: From BET desorption method

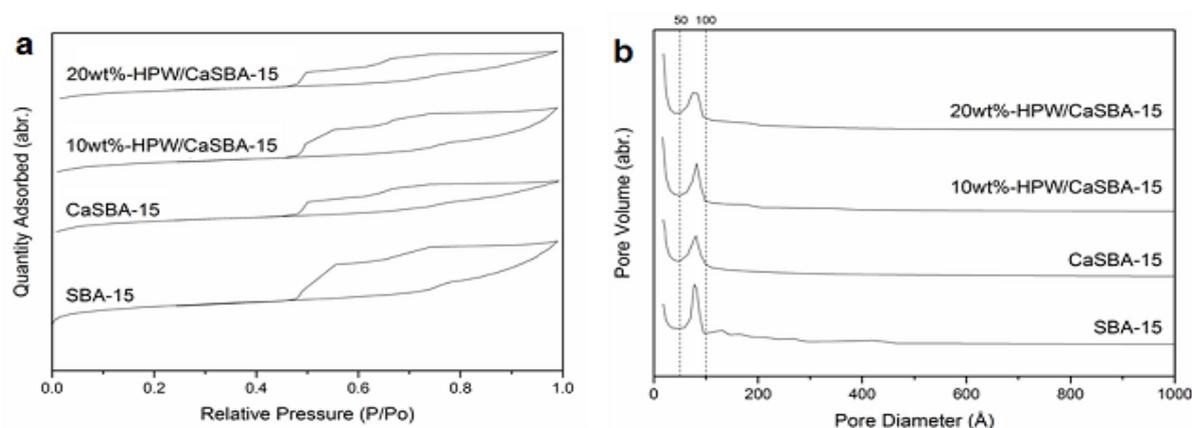
<sup>b</sup>: From the difference between total surface area to micropore surface area (t-plot method)

<sup>c</sup>: From BJH desorption method

<sup>d</sup>: From the difference between total pore volume to micropore volume (BJH Desorption method)

Evidently, all of the modified catalysts exhibited high surface areas (564 – 629 m<sup>2</sup>g<sup>-1</sup>) with large amount of uniformed mesopores (58 – 63 Å) with narrow pore size distributions (50 – 100 Å), as shown in figure 3 (b). As shown in figure 3 (a), IUPAC Type IV isotherms and type H1 hysteresis loops were found for all materials, thus verifying their mesoporous nature [23]. Such observation

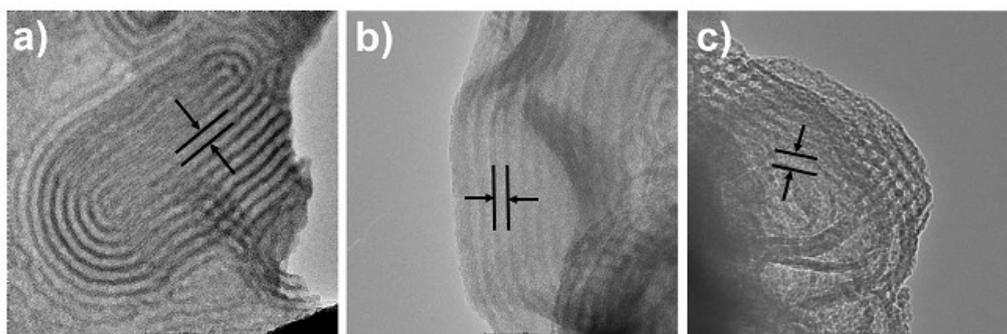
verified the retention of highly uniform mesopores channels even after the two steps modifications. Quantitatively, as seen in Table 1, high mesopores contribution on both areas (76%) and volumes (91%) for HPW/CaSBA-15 has further strengthened such claim. With respect to SBA-15, the decreases in the total surface areas and average pore sizes were observed for all the modified catalysts. The decreases were found to be more significant with further modification performed on SBA-15. As such, the observation could be attributed to the effect of the alternation on the surface characteristic of the supports [24]. For such phenomenon, it was suggested that inner pore coating of calcium or calcium oxides could have formed, causing wall thickening effect on the SBA-15. Further pore narrowing observed could be attributed to the functionalization using HPW, whereby we deduced the acid-base reaction could have occurred between the basic CaO and HPW on SBA-15 surfaces.



**Figure 3.** a) Nitrogen adsorption-desorption isotherms and b) BJH pore size distribution of SBA-15, CaSBA-15, 10wt%-HPW/CaSBA-15 and 20wt%-HPW/CaSBA-15

### 3.2. Structural analysis

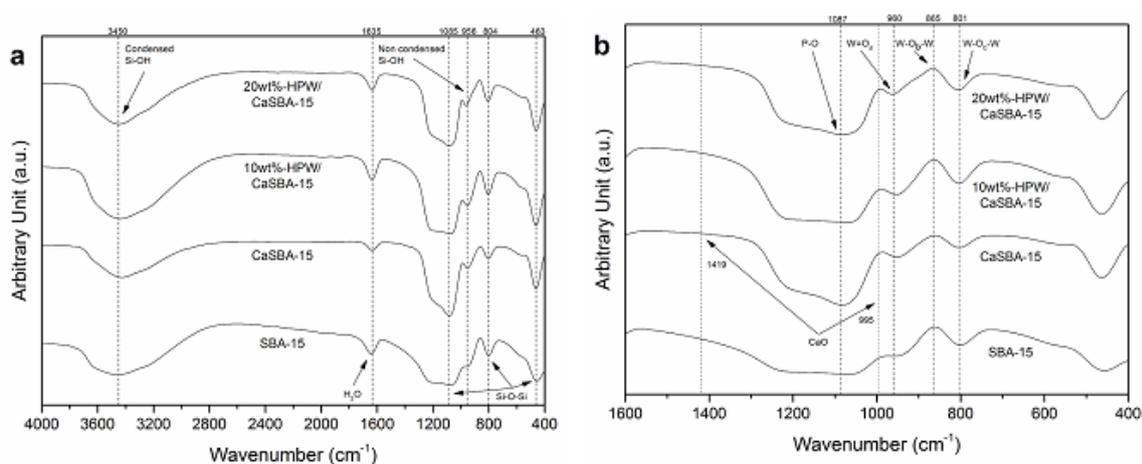
As shown in figure 4, long, continuous mesopores were easily noticeable in all three HRTEM images of the modified materials. It was observed that the undisrupted long uniform mesopores of SBA-15 was preserved even after 2 steps modifications [25]. At high magnification (195,000 X), the uniformity of the mesopores could be recognized. At the same time, the average mesopores sizes as predicted by BJH pore size analysis were justified. In fact, the trend of reduction of measured pore sizes were found to be in agreement with the trend showed in Table 1. These HRTEM images further strengthen the argument that the deposition or modification of SBA-15 with calcium oxide and later HPW acid actually occurred within these mesopores rather than on the externally available surface areas. No agglomeration of foreign particles could be detected, suggesting that well dispersion of both calcium oxide and HPW were achieved via the 2-step post impregnation method.



**Figure 4.** HRTEM images of a) CaSBA-15, b) 10wt%-HPW/CaSBA-15 and c) 20wt%-HPW/CaSBA-15 at magnification of 195,000X at 200kV

### 3.3. Chemical analysis

The FTIR scans ( $400 - 4000 \text{ cm}^{-1}$ ) for all materials were presented in figure 5 for the detection of characteristic bands of SBA-15, calcium oxides and HPW. In figure 5a, characteristic peaks attributed to Si-O-Si in the condensed silica network of SBA-15 could be identified. Specifically, these peaks include broad band of asymmetric stretching of Si-O-Si ( $1085 - 1220 \text{ cm}^{-1}$ ), symmetric Si-O-Si stretching ( $804 \text{ cm}^{-1}$ ), bending vibration of Si-O-Si ( $463 \text{ cm}^{-1}$ ), condensed Si-OH ( $3450 \text{ cm}^{-1}$ ) and non-condensed Si-OH ( $956 \text{ cm}^{-1}$ ) [26]. The characteristic bands of Keggin structured HPW, including asymmetric P-O ( $1087 \text{ cm}^{-1}$ ), terminal asymmetric oxygen  $\text{W}=\text{O}_d$  ( $960 \text{ cm}^{-1}$ ), corner shared asymmetric oxygen  $\text{W}-\text{O}_b-\text{W}$  ( $885 \text{ cm}^{-1}$ ) and edge shared oxygen  $\text{W}-\text{O}_c-\text{W}$  ( $801 \text{ cm}^{-1}$ ) could also be identified from figure 5b [27].



**Figure 5.** a) Full and b) detailed FTIR spectra of SBA-15, CaSBA-15, 10wt%-HPW/CaSBA-15 and 20wt%-HPW/CaSBA-15

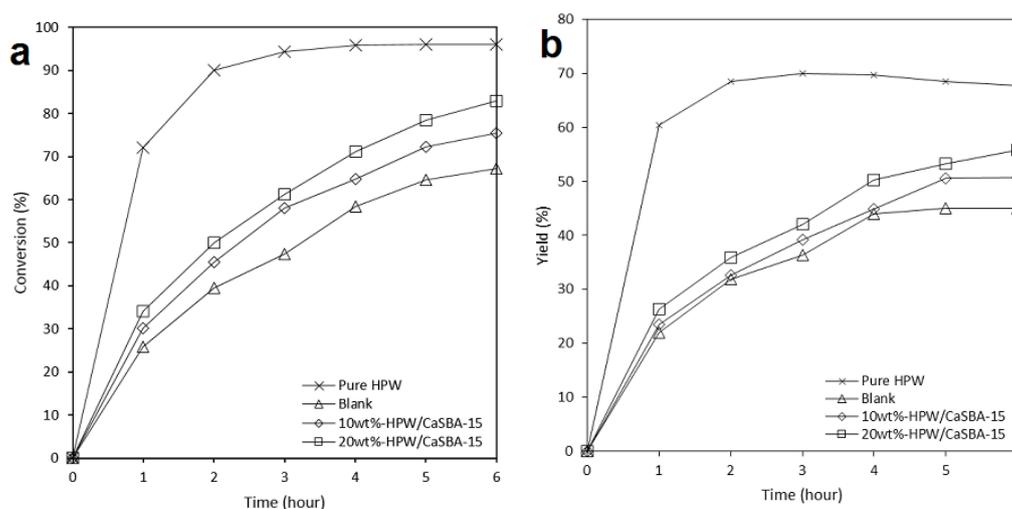
Certainly, the detection of calcium oxide associated bands was of utmost interest for verification of the CaO formation as claimed. Due to crystal lattice vibration, CaO attributed bands could be detected sharply at  $3640 \text{ cm}^{-1}$ ,  $1000 \text{ cm}^{-1}$ ,  $877 \text{ cm}^{-1}$  and broadly at  $1419 \text{ cm}^{-1}$  and  $450 \text{ cm}^{-1}$  [28]. To our best effort, sharp band at  $995 \text{ cm}^{-1}$  and broad band at  $1419 \text{ cm}^{-1}$  were identified and labelled in figure 5b. Remarkably, obvious bands changes of these two bands were observed when comparing pure SBA-15 and CaSBA-15. In fact, when compared to SBA-15, CaSBA-15 showed band intensity increment from the broad band between  $1600$  and  $1300 \text{ cm}^{-1}$  and sharp band at  $995 \text{ cm}^{-1}$ . These two findings clearly indicated the possible formation of CaO. Curiously, the intensity of sharp CaO band at  $995 \text{ cm}^{-1}$  dropped when HPW was impregnated. It was proposed that the basic CaO would react with the acidic HPW to form insoluble salt. Should this happened, the amount of available CaO anchoring sites and hence the intensity of such band would be reduced. In agreement with the observation, it was very likely that the CaHPW salts were formed as intended as in the proposed scheme (figure 2).

### 3.4. Catalytic performance and reusability

Collective catalysts performances of each synthesized catalysts were illustrated in figure 6. From figure 6a, it was noted that the homogeneous HPW achieved very high lauric acid conversion (approximately 97%) in about 3 hours, while without any catalyst at all (blank), relatively low conversion were detected (59%) at the end of the experiment run. At the same time, both HPW impregnated catalysts showed lauric acid conversion in between the homogeneously catalysed and blank experiment runs (73% for 10wt% and 81% for 20wt%-HPW/CaSBA-15). Certainly, these two catalysts showed improvement on the lauric acid conversion compared to that of the un-catalysed run with only small amount of HPW acid impregnated on them (up to 20wt%). Next, the monolaurin yield profiles in figure 6b showed improvement in the monolaurin selectivity when these catalysts were used. Undoubtedly, highest monolaurin yield (68%) was achieved with the use of pure homogeneous

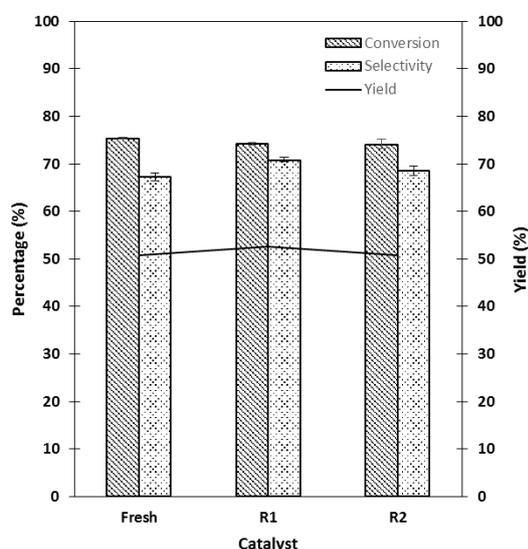
HPW. However, it was mainly due to the high lauric acid conversion (97%) and further esterification to dilaurin (24% selectivity) and trilaurin (9% selectivity).

In contrast, when 10wt%-HPW/CaSBA-15 was used, the selectivity of monolaurin, dilaurin and trilaurin were calculated to be 67%, 33% and 0%, respectively. Interestingly, no trilaurin could be detected with the use of heterogeneous catalyst. That is the similar for the case of 20wt%-HPW/CaSBA-15, too. Due to the mesopores, the formation of the much larger trilaurin could face steric hindrance and thus limiting its formation within the pore. As such, the size limiting role of SBA-15 came into effect in improving the selectivity towards monolaurin. The hindrance of trilaurin formation was achieved when HPW/CaSBA-15 catalysts were used. The selectivity improvement is undoubtedly beneficial to the research on selective esterification of glycerol with lauric acid.



**Figure 6.** a) Lauric acid conversion profiles and b) monolaurin yield of Pure HPW, 10wt%-HPW/CaSBA-15, 20wt%-HPW/CaSBA-15 and blank (control)

While the strong catalysing power of HPW incorporated materials were commonly known, their reusability were not always assuring. As the most important investigation in this study, the reusability of HPW/CaSBA-15 catalysts was discussed next. To exemplify the stability and reusability of the material synthesized, 10wt%-HPW/CaSBA-15 was chosen for the reusability test in this section. The monolaurin selectivity and yield of fresh and recycled catalysts were plotted in figure 7.



**Figure 7.** Lauric acid conversion, monolaurin selectivity and yield of the fresh and recycled 10wt%-HPW/CaSBA-15

When compared to figure 1, 10wt%-HPW/CaSBA-15 showed superior reusability up to at least 2 cycles while 40wt%-HPW/IM lost most of its catalytic performance right after the first recycle. 10wt%-HPW/CaSBA-15 demonstrated almost unchanged lauric acid conversion, monolaurin selectivity and also monolaurin yield up to the second recycle (R2). Such results were truly exciting as it provided direct evidence to the enhanced reusability and stability of the catalyst. It also further reinforced the argument of strong anchoring of HPW acid sites to the SBA-15 via calcium-bridge as proposed in figure 2. Without strong interaction, HPW acid would have been washed away from the support during the preparation phase before they can even be tested. With the strong interaction between SBA-15 and HPW via the calcium bridge, the reusability of the catalyst was greatly enhanced without compromising the catalytic performance.

#### 4. Conclusions

By using the novel two-steps calcium modification and HPW functionalization, the highly active and selective yet reusable heterogeneous catalyst for esterification of glycerol was successfully synthesized. The reusability of the modified catalysts, HPW/CaSBA-15 was elucidated by the repeat usage of the recycled catalysts up to two runs and almost no change in terms of fatty acid conversion and monoglyceride yield was observed. When compared to the HPW incorporated SBA-15, the newly developed catalyst showed significant improvement in terms of reusability. Such reusability was attributed to the strong interaction between the support and HPW acid sites via the calcium-bridging, as illustrated in Fig. 2. Also, the formation of insoluble calcium HPW acid salt within the SBA-15 minimize the possible leaching into the polar reaction matrix, which have been a major issue in both research and industries.

#### Acknowledgments

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