Conversion of a Variety of High Free Fatty Acid Containing Feedstock to Biodiesel Using Solid Acid Supported Catalyst

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Abstract: The present study explores the use of silicotungstic acid anchored to mesoporous siliceous support, KIT-6, as a catalyst to produce biodiesel. Silicotungstic acid loaded KIT-6 was synthesized and the physicochemical properties were characterized using scanning electron microscopy, surface area and pore size distribution analyzer, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and inductively coupled plasma – optical emission spectroscopy techniques. Efficiency of the silicotungstic acid loaded KIT-6 in the production of biodiesel from a variety of high free fatty acid containing feedstock was then evaluated. The composition of free fatty acids in all the feedstock oils (algae oil, coffee oil, palmitic acid and used cooking oil) and their biodiesel resulting from the feedstock were also analyzed. Compared with other solid acid catalysts, the resulting materials show stable and highly efficient catalytic performance in biodiesel production with the highest conversion reaching 99%. A sample containing 26 wt% of silicotungstic acid supported on KIT-6 was found to be the most active catalyst for esterification at 70 °C whilst stirring constantly, with an alcohol/acid volume ratio of 2 and 1.5 wt% loading catalyst for 3 h. Furthermore, the catalyst was reused for four cycles indicating recyclability of the catalyst.

Keywords: mesoporous • high free fatty acid • esterification • coffee oil • algae oil • biodiesel

1. Introduction

Global production of biofuels is growing steadily, will continue to do so and the importance of biofuel cultivation in developing countries has been thoroughly discussed recently (Duvenage *et al.*, 2013). Production of biodiesel from non-edible sources of oil such as crude palm oil (Kansedo *et al.*, 2008), animal fats (Canakci and Van Gerpen, 2001), waste cooking oil (Wang *et al.*, 2007) and algae oil (Demirbas and Fatih Demirbas, 2011) has been studied. Waste cooking oil, in particular, has received considerable interest due to problems encountered in its disposal as it can clog sewer and septic systems and cause corrosion of certain materials (Sheinbaum-Pardo *et al.*, 2013), cost of disposal and the high volume rate at which it is generated. Moreover, these feedstocks contain high amount of free fatty acids (FFAs) that make the conversion difficult (Hayyan *et al.*, 2014). Developing new cheaper

catalysts to convert high FFA feedstock will not only solve the issue of disposal of waste cooking oil but will also enhance the overall economics of biodiesel production (Navajas *et al.*, 2013). Recent developments to lower the cost of biodiesel employ catalysts that can be re-used, such as heterogeneous catalysts which are in different phase from both reactants and products. Using these catalysts simplifies the purification process and thereby lowers the overall cost of biodiesel production (Aransiola *et al.*, 2014; Vyas *et al.*, 2010). These studies have also identified various drawbacks of using homogeneous acid catalyzed esterification such as the formation of water as a by-product and very slow reaction kinetics, compared to traditional transesterification (Gui *et al.*, 2008). There are other diverse types of catalysts which could be employed in esterification of high FFA oils (Ayodele and Dawodu, 2014; Fang *et al.*, 2013) but this study focuses on solid acid impregnated catalysts, particularly heteropoly acids (HPAs), because of their innate chemical resistance to moisture (Sharma *et al.*, 2011). Also, HPAs can convert feedstock containing high amount of FFAs, which enables their use with low cost feedstocks such as used cooking oil and other non-edible vegetable oils (Endalew *et al.*, 2011). HPAs are very strong Brönsted acids that are comparable to or stronger than conventional acids such as HCl, H₂SO₄, HClO₄, zeolites and acidic resins (Zhang *et al.*, 2010). Despite these advantages HPAs have very low surface area <10 m²/g in solid state and are essentially of low porosity with very few acid sites available for reaction with hydrocarbons (Gucbilmez *et al.*, 2012). Other problems associated with HPAs are diffusion limited selectivity of reacting species namely diglycerides and monoglycerides, polar interaction between solvent and catalyst, deactivation, leaching (Endalew *et al.*, 2011). The issue of solubility can be addressed by converting the HPA into a salt (Srilatha *et al.*, 2012), or by introducing a supporting vector in form of a mesoporous matrix such as SBA 15, MCM 41, and MCM 48 silica. Table 1 gathers and classifies some of the similar mesoporous catalysts used by previous works on the esterification of several oils. It also provides the important conclusions reached for each catalyst.

KIT-6 (Korean Institute of Technology-6) is a specific mesoporous material that exhibits a three-dimensional cubic Ia3d symmetric structure with an interpenetrating bi-continuous network of channels (Vinu *et al.*, 2008). The unique 3D channel network in this structure provides direct access to reactant species without pore blockage (Rossinyol *et al.*, 2007). Pure siliceous KIT-6 material is an electronically neutral framework and is consequently devoid of acidic or basic sites. In order to impart acidity or basicity, metal atoms can be exchanged into the framework either by grafting or by direct synthesis. In this study, silicotungstic acid was anchored onto the surface of KIT-6 framework, which was synthesized in the laboratory and the catalytic activity of the resulting solid acid catalyst in esterification reactions was evaluated. KIT-6 loaded with varying concentrations of STA (0%, 10%, 15%, 30%, 40% by weight) was used to esterify algae oil (very high FFA content), coffee oil, used cooking oil and palmitic acid (model compound as control for comparison) resulting in the conversion of FFA into methyl esters. The aim of this work was to develop a catalyst with the capability of tolerating a wide range of feedstock properties.

2. Experimental Section

The preparation and characterization of the solid acid catalyst, followed by catalytic studies to investigate its use and recyclability for transesterification of various feedstocks into biodiesel is provided below.

2.1 Materials and Methods

Pluronic P123 triblock co-polymer [poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)] with molecular weight of 5800 (EO20PO70EO20) and n-butyl alcohol (n-BuOH) were Sigma-Aldrich and VWR International respectively and used as the structure directing agent and co-surfactant, respectively. Tetraethylorthosilicate (TEOS) was used as a source of silicon for the synthesis of KIT-6. Hydrochloric acid (35 wt%) was used as a co-solvent for the synthesis of mesoporous 3D cubic KIT-6 molecular sieves. Silicotungstic acid was used for immobilization on the mesoporous framework. All chemicals were of reagent grade or better and were purchased from VWR International. Used cooking oil (UCO) was obtained from a local restaurant. UCO was subjected to a simple pre-treatment which consisted of filtration of the solid particles and followed by heating to 100 °C and maintaining for 15 min to remove any moisture. Temperature was then maintained at 70 °C. Coffee oil was extracted from spent coffee grounds using a solvent (hexane) extraction method that was developed earlier (Kondamudi *et al.*, 2008). Algae oil was obtained from Pacific propellants, Inc. Palmitic acid was used as a model compound. Palmitic acid and other reagents were analytical or higher grade and were used without further purification. Deionized water was used throughout the experimentation. After the esterification reaction, the STA-D catalyst was separated, washed with hexane and dried at 100°C to remove any water molecules that could interfere with its catalytic activity. The resulting oil-free used catalyst powder was then reused as catalyst for a new reaction under the same conditions. There is a certain degree of difficulty involved in recovering all of the catalyst from the filter due to the small quantities involved. However, this is not expected to be a concern at larger scales as amount of materials recovered is expected to be higher.

2.2 Synthesis of catalyst

KIT-6 was synthesized by following a previously published protocol (Kim *et al.*, 2005). Pluronic P123 (4 g) was added to water (144 g) and 35% HCl (7.9 g). After stirring for 4 h, a clear solution was obtained. n-Butanol (4 g) was then added and the stirring was continued for 1 hour. TEOS (8.6 g) was subsequently added to the solution. The resulting mixture was stirred for 24 h at 35 °C. The synthesis was carried out in a closed polypropylene bottle. Following synthesis, the mixture was aged at 100 °C for 24 h under static hydrothermal conditions. The precipitated material was filtered while hot, without washing and then dried at 100 °C for 12 h in air. The dried solid material was crushed to obtain fine powder which was calcined at 540 °C in air for 24 h to remove the template. To this framework, STA was loaded at various concentrations of 5%, 10%, 15%, 20% and 30%. The catalysts with different STA loadings were prepared by suspending a known amount of an aqueous solution of STA (i.e. 'x' g

of STA in 20 mL distilled water) per 1g of KIT-6 support. An IKA C-MAG HS7 hot plate stirrer with an ETS-D5 temperature control feedback was used to maintain reaction conditions. The mixture was stirred for 2 h at 500 rpm at room temperature and was followed by evaporation to dryness in a rotary evaporator. The dried samples were then maintained at 100 °C for 12 h in an oven, further powdered and calcined at 600 °C in air for 4 h.

2.3 Analytical methods

The specific surface area of the catalyst/ support material was measured using an Autosorb 2010™ surface area and pore size analyzer. Nitrogen adsorption–desorption isotherms were measured in liquid nitrogen using a Micromeritics ASAP 2010 system. The morphology was characterized using a Hitachi S-4700 scanning electron microscope (SEM) using a standard secondary electron detector at 11.0 kV. Chemistry was confirmed using Fourier transform infrared spectroscopy (FTIR). The separate samples were ground with KBr and pressed into thin wafers to measure the IR adsorption of the groups. X-ray diffraction patterns (XRD) were obtained using PANalytical X'Pert Pro X-ray diffractometer with Cu K α radiation. A PHI 5600 X-ray photoelectron spectrometer (XPS) with a monochromatic Al source was used at 14 kV and 300 W to identify the surface chemistry of the catalyst. Perkin Elmer OPTIMA 8000 inductively coupled plasma – optical emission spectroscopy (ICP-OES) was used to quantify the amount of acid exchanged with the framework. The wavelength chosen was 207.91 nm and limit of detection for tungsten was 7 ppb. The W-ion concentration was used to calculate the amount of acid exchanged with the framework. For this purpose, STA-D (0.1 g) catalyst was accurately measured and digested with 5M NaOH solution (15 mL) for 4 h. The solution was then diluted to a known volume and was analyzed for tungsten using ICP-OES. Amount of STA that leaches from the KIT-5 framework material into the reaction mixture was also evaluated using ICP-OES analyses. For this purpose, STA-D (1 g) catalyst was mixed with triple distilled water (10 mL) and was refluxed for 16 h. The leachate was then analyzed for tungsten ion concentration. Control experiments were conducted using 0.4 g of framework-free STA. The identities and relative proportions of fatty acids in the methyl ester product were determined using a Shimadzu GC QP-2010 gas chromatograph mass spectroscopy (GC-MS) equipped with a SHR-5XLB capillary column (25 mm thickness x 30 m length) and an electron ionization detector (70eV) using helium as the reagent gas. A temperature gradient was selected such that the temperature rose from 100 °C to 240 °C at the rate of 1.5 °C per minute.

2.4 Esterification methodology

STA was incorporated as a heteroatom into the KIT-6 framework to impart catalytic activity and use it as a solid acid catalyst for esterification reactions. Unloaded KIT-6 framework, STA-A, STA-B, STA-C and STA-D were evaluated for the effectiveness in converting algae oil, used cooking oil, coffee oil and palmitic acid into biodiesel.

Ten grams of oil and a catalyst concentration of 1.5 wt% based on the mass of oil was used. This concentration was considered to be the minimum requirement for the esterification of the free fatty acids. Methanol was employed in a 1:2 v/v ratio and the reaction temperature was kept constant at 70 °C. After completion of the reaction, a 24 h pour-off time allowed for the complete separation of an upper ester layer from a lower glycerol layer. The upper layer was collected and excess methanol was removed using rotary evaporation at 60 °C, under moderate vacuum. After alcohol recovery, the methyl ester was transferred into a clean separatory funnel. It was washed gently with warm tap water and 10% tannic acid solution as a purification step. The ester phase was analyzed by gas chromatography to determine the yield of fatty acid methyl esters (FAMES). All esterification experiments were conducted in duplicates. The AOCS official method CA 5a-40 was used to analyze the FFA content in the oils by titrating against 0.1 N NaOH.

3. Results and Discussion

The results from the characterization of the catalyst using X-ray diffraction, Brunauer–Emmett–Teller (BET)/N₂ physisorption, scanning electron microscopy with energy dispersive spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy are described below. The stability as well as activity of the catalyst were also tested and is also reported below.

3.1 Catalyst characterization

SEM images of STA loaded KIT-6 are shown in Figures 1a-1d. The crystals were of large irregular shape and the morphology was rough. It was observed that the STA was well-dispersed on KIT-6, and its spherical shape was retained as seen in Figure 1b. The images obtained were similar to previously reported SEM images of the KIT-6 mesoporous support confirming the formation of the KIT-6 template (Dai *et al.*, 2010; Gao *et al.*, 2011; NuLi *et al.*, 2010).

Surface area was quantified using the nitrogen absorption/desorption multipoint Brunauer–Emmett–Teller (BET) method. The surface area of materials was relatively high confirming the suitability of these materials for heterogeneous catalysis. Surface area of the catalysts decreased with an increase in acid loading and such behavior has been previously documented (Hamoudi and Kaliaguine, 2003; He *et al.*, 2005). The results from the quantification of elemental W present in the samples, conducted using an inductively coupled plasma optical emission spectrometer, were used to calculate the amount of acid that was incorporated into the framework successfully. Table 2 shows the surface area of the catalysts and the amount of acid that was loaded on the silica framework which is represented as percent acid exchanged with the framework.

The N₂ adsorption–desorption isotherms of KIT-6 framework, STA loaded KIT-6 catalysts and pure STA is presented in Figure 2a-2f. As seen in this figure, the isotherms can be characterized as type IV (Rossinyol *et al.*, 2007). All materials exhibit a high degree of structural ordering, as indicated by the steep capillary condensation step in their respective adsorption isotherm. As per IUPAC classification,

the presence of a sharp capillary condensation step with an H1 hysteresis loop indicative of well-defined cylindrical pores. It is usually difficult to conserve the mesostructure of composite materials as a result of pore filling during impregnation. Also, the pore size distribution obtained from the BET measurements of catalyst STA-D is given in Figure 3. KIT-6 has a narrow pore distribution centered at 7.5nm and is in agreement with the distributions of KIT-6 and other types of mesoporous materials reported earlier (Jiao *et al.*, 2005; Takahashi *et al.*, 2000; Wang *et al.*, 2001).

The crystallographic XRD pattern provided in Figure 4 indicates that the solid acid is exchanged with the framework. Also, the characteristic pattern for STA starts to become more apparent with increasing STA content in the STA-exchanged samples, and is obvious for STA-C and STA-D samples. Thus, the crystalline structure of STA was not destroyed during the impregnation process.

Figure 5 shows the infrared spectra. The characteristic bands of Keggin-type mesoporous catalyst were observed at 1083, 968 and 805 cm^{-1} . The IR absorption peaks at 805 cm^{-1} (Morey *et al.*, 2000) and 1083 cm^{-1} (Damyanova *et al.*, 2003; Morey *et al.*, 2000) are due to Si-O-Si vibrations of silica framework of KIT-6. The absorption peak at 968 cm^{-1} is due to the stretching vibrations of Si-O in the Si-O—R⁺ groups (Damyanova *et al.*, 2003). This band is generally regarded as evidence of the metal cation incorporation into the framework of mesoporous silicates. The Si-O-H stretching vibration is clearly evident at 977 cm^{-1} (Morey *et al.*, 2000) even after calcination.

The wide scan XPS spectrum obtained on the STA-D catalyst confirmed that W was present on the surface following the acid impregnation process. As shown in Figure 6, there was a large O 1s peak that was detected at ~533.1 eV, which corresponds to Si-O bond present in SiO₂ (Albuquerque *et al.*, 2008).

3.2 Conversion and Yield

The acid number of the feedstock and products were determined and was subsequently used to calculate the conversion of FFA to FAME (Hayyan *et al.*, 2010). After a relatively short reaction time of 3 h, the conversion was found to be proportionate to the amount of STA loaded on to the catalyst. The influence of HPA loading on the catalytic performance is given in Table 3. The results obtained were consistent with our earlier work on the influence of HPA concentration on the biodiesel conversion (Bala *et al.*, 2014). From Table 3, it can be observed that the conversion increased significantly with increasing STA loading, and the highest conversion of ~99% was obtained with UCO and palmitic acid using STA-D. Several research groups have previously attempted to produce biodiesel using heterogeneous solid acid catalysts. Tungstophosphoric acid, molybdophosphoric acid and STA immobilized on SBA-15 were used in the esterification of palmitic acid and conversions greater than 95% were observed (Tropecêlo *et al.*, 2010). However, since the pore structures are different in SBA-15 and KIT-6, a different HPA was used in the current study. The optimal catalyst composition that allows the achievement of maximum catalyst performance was also evaluated and conversions greater than 96% were observed. Not surprisingly, pure HPA, H₃PW₁₂O₄₀.6H₂O (PW₁₂) was used in the

esterification of waste cooking oil using a 3.75% weight ratio of catalyst to oil and 70:1 ratio of methanol/oil, at 65°C for 12 h, and a maximum conversion of 95.8% was observed (Cao *et al.*, 2008). Comparatively, in the present study, the maximum ratio of catalyst to oil used was 1.5% by weight. It is also important to note that the amount of HPA involved in the reaction itself was lesser than the amount used in the above study. MCM-41-supported heteropoly acids (HPAs) have also been used as catalysts in the gas-phase esterification of acetic acid and 1-butanol (Verhoef *et al.*, 1999). These catalysts resulted in a 95% conversion at 110 °C and the fact that MCM-41-supported HPA was more active than pure HPA was also evident. Mesoporous silica based catalysts functionalized with propyl sulfonic acid (SO₃H) have been reported to have good catalytic activity in esterification of virgin and unrefined oils (Mbaraka *et al.*, 2006; Melero *et al.*, 2009). It is known that previous studies have shown good activity, but even in those successful cases, the process conditions were not optimal; due to either high reaction temperature, long reaction times or the amount of catalyst required. However, in the current work, based on the results obtained from using STA-D, the conversion of FFA to FAME was greater than 96% with all feedstocks and this was obtained at shorter reaction times in comparison with similar catalysts while also enabling greater flexibility with feedstocks for biodiesel production.

The gas chromatograms of representative samples are shown in Figure 7. The retention times of the separated compounds contained in the sample match the retention times of the FAMES and FFAs found in the GC-MS database. Fatty acids and their corresponding methyl esters are labeled. The chromatograms show the various types of FAMES that were produced, making it possible to differentiate the feedstock from the biodiesel sample. Results showed that each type of biodiesel contained a different composition of FAME that depends on the composition of the starting feedstock material. The dominant fatty acid (~60%) in UCO was octadecanoic acid (18:1), which was converted to its methyl ester as shown in Figure 7a. Algal biodiesel was found to contain a significant proportion of mono and poly unsaturated fatty acid methyl esters as seen in Figure 7b. The dominant fatty acid (~50%) in algae oil was octadecanoic acid (18:0), was found to be converted to its methyl ester. Figure 7c shows the GC-MS results obtained from coffee oil feedstock and the biodiesel resulting from it. C16–C20 methyl esters of fatty acids were found to be present. Coffee biodiesel consists of both saturated and unsaturated methyl esters. The dominant fatty acids in coffee oil were hexadecanoic acid (16:0) and octadecanoic acid (18:0), which were seen to be converted to methyl esters. Palmitic acid was used as a feedstock and acted as control. The dominant fatty acid (~100%) in palmitic acid was hexadecanoic acid (16:0), which was found to be converted to its methyl ester as seen in Figure 7d.

To estimate the amount of biodiesel formed upon completion of the reaction, the biodiesel weight yield relative to the initial amount of feedstock, was calculated using a previously established method (Hayyan *et al.*, 2010). The yield obtained when each catalyst was used is presented in Table 4. The yield obtained with algae oil was significantly lower than that obtained with coffee, UCO and palmitic acid. It is assumed that fatty acid neutralization might be the reason for the loss in yield. Studies

conducted on other mesoporous materials such as SBA-15 and MCM-41 have reported similar yield when other oils were used as feedstock (Brahmkhatri and Patel, 2011; Gucbilmez et al., 2012). 12-phosphotungstic acid (PTA) impregnated on four supports namely silica, alumina, hydrous zirconia, and activated carbon were used for the production of biodiesel from low quality canola oil which contained up to 20 wt% FFA. Under optimized conditions at 200 °C, 1: 9 oil to alcohol molar ratio and 3 wt% catalyst loading, an ester yield of 90 wt% was obtained (Kulkarni et al., 2006). Usually, heterogeneous catalysts are synthesized with highly pure metal oxides for better catalytic properties. On the contrary, STA-D as a solid acid catalyst also exhibited comparable catalytic properties, indicating that solid acid mesoporous catalysts are active candidates for transesterification and esterification reactions due to their high acidity. One outstanding advantage with using STA-D is the high conversion and its ability to use a wide range of high free fatty acid containing feedstock materials. In addition, it was found that this process requires lower amount of catalyst, could operate at a lower temperature and required a simpler purification procedure in comparison to similar studies using HPA loaded mesoporous materials that have been discussed above. Also, the use of STA-D catalyst did not lead to the formation of soap, thereby avoiding the neutralization of FFAs. Further, this study shows that elevated temperatures and pressures are not essential for heterogeneously catalyzed transesterifications. Furthermore, it is believed that the currently investigated catalyst can improve the sustainability of the biodiesel production process because the problems associated with the use of homogeneous catalysts have been eliminated successfully. The growing interest to develop an industrial scale production process based on solid acid catalysts is justified by the economics of the process. The use of similar reaction conditions, easier product recovery, and better performance than homogeneous catalysts suggest that STA-D could be a viable catalyst for use on a larger scale. However, the production cost of STA-D is still significantly higher than that of homogeneous catalysts. But further research and process optimization, and potential savings resulting from the recycling of the catalyst and prevention of unwanted processes such as soap formation, could lead to its application on an industrial scale.

4. Recycling studies

Besides activity, another critical point to examine is the catalyst activity loss and reusability. One of the main disadvantages of homogeneous catalysts is that they cannot be recovered. So, in the present study, the catalyst was evaluated to study its efficiency and reusability. The used catalyst was re-tested maintaining a 1.5 wt% catalyst quantity. The results of the recycling studies conducted on UCO have been summarized in Figure 8. This is in agreement with previous studies that have demonstrated that HPAs and other solid acids anchored to mesoporous supports could be recycled and have been proven to have good recyclability (Ren et al., 2010; Sofia et al., 2009; Zhang et al., 2013). After four cycles of successive re-use, the conversion obtained decreased by 26%. According to these results, after each recycle the catalyst appears to have lost some activity, indicating that there is some small degree of acid leaching from the catalyst, and, hence, minor deactivation. Previous studies on the

leaching of the HPA's from frameworks with Keggin structure suggest that, since these frameworks have the ability to maintain their structure, the amount of leaching of HPA's from these frameworks is minimal (Alsalmeh *et al.*, 2008). In other words, the large surface area of the support enhances stability of the catalysts at temperature range within stability range of the bulk HPA. Leaching can be avoided by aging the catalyst at a higher temperature, but the overall activity of the catalyst may then be compromised (Alsalmeh *et al.*, 2008). Several other studies have reported mild leaching with HPA's loaded on mesoporous supports and the catalysts were recycled 3 times with similar minor loss of activity (Narasimharao *et al.*, 2007; Xu *et al.*, 2008b). $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ta}_2\text{O}_5$ was tested for its reusability in the simultaneous esterification of myristic acid and transesterification of tripalmitin and the yield decreased by 22%(Xu *et al.*, 2008a). This is in agreement with the current results, taking into account the experimental error and difference in the framework used. It is probable that the observed catalyst deactivation was also the result of site blockage by adsorbed intermediates or product species. Although the mild leaching of the active species looks inescapable, experiments involving the use of the solid catalyst, in the form of pellets, for longer operating times, would be helpful to determine if leaching is a serious issue for the stability and commercialization of the catalyst. This is an area that has scope for further research.

5. Conclusions

Biodiesel production from algae, coffee and used cooking oils with a high content of FFA was investigated using acid supported mesoporous catalysts. Mesoporous silicate material (KIT-6) was successfully synthesized and STA was exchanged with the framework. Analysis of physical properties of the synthesized catalysts substantiated the formation of catalysts with high surface area, their morphological properties and mesoporosity. The present work demonstrates that the synthesized solid acid catalyst could be used for single step esterification of high FFA containing oils such as coffee oil, used cooking oil and palmitic acid. More importantly, the catalyst was found to be stable after calcination, esterification and recycling, which is essential for commercial applications of catalysts. It was also observed that the conversion efficiency is strongly affected by silicotungstic acid concentration in the catalyst and a silicotungstic acid concentration of ~26 wt% favors the near completion of solid acid catalyzed esterification process.

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7. References

Abreu, F.R., Alves, M.B., Macêdo, C.C.S., Zara, L.F., Suarez, P.A.Z., 2005. New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterification reaction. *Journal of Molecular Catalysis A: Chemical* 227, 263-267.

Albuquerque, M.C.G., Jiménez-Urbistondo, I., Santamaría-González, J., Mérida-Robles, J.M., Moreno-Tost, R., Rodríguez-Castellón, E., Jiménez-López, A., Azevedo, D.C.S., Cavalcante Jr, C.L., Mairesles-Torres, P., 2008. CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. *Applied Catalysis A: General* 334, 35-43.

Alsalmé, A., Kozhevnikova, E.F., Kozhevnikov, I.V., 2008. Heteropoly acids as catalysts for liquid-phase esterification and transesterification. *Applied Catalysis A: General* 349, 170-176.

Aransiola, E.F., Ojumu, T.V., Oyekola, O.O., Madzimbamuto, T.F., Ikhu-Omoregbe, D.I.O., 2014. A review of current technology for biodiesel production: State of the art. *Biomass and Bioenergy* 61, 276-297.

Ayodele, O.O., Dawodu, F.A., 2014. Conversion of *Calophyllum inophyllum* Oil with a High Free Fatty Acid Content to Biodiesel using a Starch-Derived Catalyst. *Energy Technology* 11, 912-920.

Bala, D.D., Misra, M., Chidambaram, D., 2014. Single step esterification of algae oil using mesoporous solid acid catalyst. *Fuel* 117, Part B, 1093-1095.

Brahmkhatri, V., Patel, A., 2011. Biodiesel production by esterification of free fatty acids over 12-tungstophosphoric acid anchored to MCM-41. *Industrial & Engineering Chemistry Research* 50, 6620-6628.

Caetano, C.S., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E., 2008. Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica. *Catalysis Communications* 9, 1996-1999.

Canakci, M., Van Gerpen, J., 2001. Biodiesel production from oils and fats with high free fatty acids. *Transactions-American Society of Agricultural Engineers* 44, 1429-1436.

Cao, F., Chen, Y., Zhai, F., Li, J., Wang, J., Wang, X., Wang, S., Zhu, W., 2008. Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid. *Biotechnology and Bioengineering* 101, 93-100.

Dai, W., Zheng, M., Zhao, Y., Liao, S., Ji, G., Cao, J., 2010. Template Synthesis of Three-Dimensional Cubic Ordered Mesoporous Carbon With Tunable Pore Sizes. *Nanoscale Res Lett* 5, 103-107.

Damyanova, S., Dimitrov, L., Mariscal, R., Fierro, J.L.G., Petrov, L., Sobrados, I., 2003. Immobilization of 12-molybdophosphoric and 12-tungstophosphoric acids on metal-substituted hexagonal mesoporous silica. *Applied Catalysis A: General* 256, 183-197.

Demirbas, A., Fatih Demirbas, M., 2011. Importance of algae oil as a source of biodiesel. *Energy Conversion and Management* 52, 163-170.

Duvenage, I., Langston, C., Stringer, L.C., Dunstan, K., 2013. Grappling with biofuels in Zimbabwe: depriving or sustaining societal and environmental integrity? *Journal of Cleaner Production* 42, 132-140.

Endalew, A.K., Kiros, Y., Zanzi, R., 2011. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass and Bioenergy* 35, 3787-3809.

Fang, D., Jiang, C., Yang, J., 2013. Preparation of Biodiesel from Castor Oil Catalyzed by Novel Basic Ionic Liquid. *Energy Technology* 1, 135-138.

Gao, T., Ji, G., Chang, X., Lin, X., Liu, J., Qamar, M., 2011. Electrochemical deposition and magnetic properties of cobalt and iron thin films on substrate of KIT-6/ITO. *J Mater Sci* 46, 5221-5226.

Georgogianni, K.G., Katsoulidis, A.P., Pomonis, P.J., Kontominas, M.G., 2009. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. *Fuel Processing Technology* 90, 671-676.

Gucbilmez, Y., Yargic, A., Calis, I., 2012. A comparative characterization of the HPA-MCM-48 type catalysts produced by the direct hydrothermal and room temperature synthesis methods. *Journal of Nanomaterials* 2012, 28.

Gui, M.M., Lee, K.T., Bhatia, S., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy* 33, 1646-1653.

- Hamoudi, S., Kaliaguine, S., 2003. Sulfonic acid-functionalized periodic mesoporous organosilica. *Microporous and Mesoporous Materials* 59, 195-204.
- Hayyan, A., Alam, M.Z., Mirghani, M.E.S., Kabbashi, N.A., Hakimi, N.I.N.M., Siran, Y.M., Tahiruddin, S., 2010. Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource Technology* 101, 7804-7811.
- Hayyan, A., Hashim, M.A., Hayyan, M., Mjalli, F.S., AlNashef, I.M., 2014. A new processing route for cleaner production of biodiesel fuel using a choline chloride based deep eutectic solvent. *Journal of Cleaner Production* 65, 246-251.
- He, N.-Y., Woo, C.-S., Kim, H.-G., Lee, H.-I., 2005. Catalytic formation of acetic anhydride over tungstophosphoric acid modified SBA-15 mesoporous materials. *Applied Catalysis A: General* 281, 167-178.
- Isahak, W., Ismail, M., Nordin, N., Jahim, J., Yarmo, M., 2011. Synthesis, Characterization and Catalytic Performance of $\text{H}_3\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ Prepared by Sol-Gel Technique. *Journal of Nanotechnology* 2011, 1-6.
- Jiao, K., Zhang, B., Yue, B., Ren, Y., Liu, S., Yan, S., Dickinson, C., Zhou, W., He, H., 2005. Growth of porous single-crystal Cr_2O_3 in a 3-D mesopore system. *Chemical Communications*, 5618-5620.
- Kansedo, J., Lee, K.T., Bhatia, S., 2008. Feasibility of Palm Oil as the Feedstock for Biodiesel Production via Heterogeneous Transesterification. *Chemical Engineering & Technology* 31, 993-999.
- Khder, A.E.R.S., Hassan, H.M.A., El-Shall, M.S., 2012. Acid catalyzed organic transformations by heteropoly tungstophosphoric acid supported on MCM-41. *Applied Catalysis A: General* 411-412, 77-86.
- Kim, T.-W., Kleitz, F., Paul, B., Ryoo, R., 2005. MCM-48-like Large Mesoporous Silicas with Tailored Pore Structure: Facile Synthesis Domain in a Ternary Triblock Copolymer-Butanol-Water System. *Journal of the American Chemical Society* 127, 7601-7610.
- Kondamudi, N., Mohapatra, S.K., Misra, M., 2008. Spent Coffee Grounds as a Versatile Source of Green Energy. *Journal of Agricultural and Food Chemistry* 56, 11757-11760.
- Kulkarni, M.G., Gopinath, R., Meher, L.C., Dalai, A.K., 2006. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry* 8, 1056-1062.
- Mbaraka, I.K., McGuire, K.J., Shanks, B.H., 2006. Acidic Mesoporous Silica for the Catalytic Conversion of Fatty Acids in Beef Tallow. *Industrial & Engineering Chemistry Research* 45, 3022-3028.
- Melero, J.A., Iglesias, J., Morales, G., 2009. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chemistry* 11, 1285-1308.
- Morey, M.S., O'Brien, S., Schwarz, S., Stucky, G.D., 2000. Hydrothermal and Postsynthesis Surface Modification of Cubic, MCM-48, and Ultralarge Pore SBA-15 Mesoporous Silica with Titanium. *Chemistry of Materials* 12, 898-911.
- Narasimharao, K., Brown, D.R., Lee, A.F., Newman, A.D., Siril, P.F., Tavener, S.J., Wilson, K., 2007. Structure-activity relations in Cs-doped heteropolyacid catalysts for biodiesel production. *Journal of Catalysis* 248, 226-234.
- Navajas, A., Issariyakul, T., Arzamendi, G., Gandía, L.M., Dalai, A.K., 2013. Development of eggshell derived catalyst for transesterification of used cooking oil for biodiesel production. *Asia-Pacific Journal of Chemical Engineering* 8, 742-748.
- NuLi, Y., Yang, J., Li, Y., Wang, J., 2010. Mesoporous magnesium manganese silicate as cathode materials for rechargeable magnesium batteries. *Chemical Communications* 46, 3794-3796.
- Park, Y.-M., Lee, D.-W., Kim, D.-K., Lee, J.-S., Lee, K.-Y., 2008. The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catalysis Today* 131, 238-243.
- Ren, Y., Yue, B., Gu, M., He, H., 2010. Progress of the Application of Mesoporous Silica-Supported Heteropolyacids in Heterogeneous Catalysis and Preparation of Nanostructured Metal Oxides. *Materials* 3, 764-785.

- Rossinyol, E., Prim, A., Pellicer, E., Arbiol, J., Hernández-Ramírez, F., Peiró, F., Cornet, A., Morante, J.R., Solovyov, L.A., Tian, B., Bo, T., Zhao, D., 2007. Synthesis and Characterization of Chromium-Doped Mesoporous Tungsten Oxide for Gas Sensing Applications. *Advanced Functional Materials* 17, 1801-1806.
- Sharma, Y.C., Singh, B., Korstad, J., 2011. Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels, Bioproducts and Biorefining* 5, 69-92.
- Sheinbaum-Pardo, C., Calderón-Irazoque, A., Ramírez-Suárez, M., 2013. Potential of biodiesel from waste cooking oil in Mexico. *Biomass and Bioenergy* 56, 230-238.
- Singh, S., Patel, A., 2014. 12-Tungstophosphoric acid supported on mesoporous molecular material: synthesis, characterization and performance in biodiesel production. *Journal of Cleaner Production* 72, 46-56.
- Sofia, L.T.A., Krishnan, A., Sankar, M., Kala Raj, N.K., Manikandan, P., Rajamohanam, P.R., Ajithkumar, T.G., 2009. Immobilization of Phosphotungstic Acid (PTA) on Imidazole Functionalized Silica: Evidence for the Nature of PTA Binding by Solid State NMR and Reaction Studies. *The Journal of Physical Chemistry C* 113, 21114-21122.
- Srilatha, K., Sree, R., Prabhavathi Devi, B.L.A., Sai Prasad, P.S., Prasad, R.B.N., Lingaiah, N., 2012. Preparation of biodiesel from rice bran fatty acids catalyzed by heterogeneous cesium-exchanged 12-tungstophosphoric acids. *Bioresource Technology* 116, 53-57.
- Takahashi, H., Li, B., Sasaki, T., Miyazaki, C., Kajino, T., Inagaki, S., 2000. Catalytic Activity in Organic Solvents and Stability of Immobilized Enzymes Depend on the Pore Size and Surface Characteristics of Mesoporous Silica. *Chemistry of Materials* 12, 3301-3305.
- Taufiq-Yap, Y.H., Lee, H.V., Yunus, R., Juan, J.C., 2011. Transesterification of non-edible *Jatropha curcas* oil to biodiesel using binary Ca-Mg mixed oxide catalyst: Effect of stoichiometric composition. *Chemical Engineering Journal* 178, 342-347.
- Tropecêlo, A.I., Casimiro, M.H., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E., 2010. Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous silica. *Applied Catalysis A: General* 390, 183-189.
- Verhoef, M.J., Kooyman, P.J., Peters, J.A., van Bekkum, H., 1999. A study on the stability of MCM-41-supported heteropoly acids under liquid- and gas-phase esterification conditions. *Microporous and Mesoporous Materials* 27, 365-371.
- Vinu, A., Gokulakrishnan, N., Balasubramanian, V.V., Alam, S., Kapoor, M.P., Ariga, K., Mori, T., 2008. Three-Dimensional Ultralarge-Pore Ia3d Mesoporous Silica with Various Pore Diameters and Their Application in Biomolecule Immobilization. *Chemistry – A European Journal* 14, 11529-11538.
- Vyas, A.P., Verma, J.L., Subrahmanyam, N., 2010. A review on FAME production processes. *Fuel* 89, 1-9.
- Wang, Y., Noguchi, M., Takahashi, Y., Ohtsuka, Y., 2001. Synthesis of SBA-15 with different pore sizes and the utilization as supports of high loading of cobalt catalysts. *Catalysis Today* 68, 3-9.
- Wang, Y., Ou, P.L.S., Zhang, Z., 2007. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy Conversion and Management* 48, 184-188.
- Xu, L., Wang, Y., Yang, X., Yu, X., Guo, Y., Clark, J.H., 2008a. Preparation of mesoporous polyoxometalate-tantalum pentoxide composite catalyst and its application for biodiesel production by esterification and transesterification. *Green Chemistry* 10, 746-755.
- Xu, L., Yang, X., Yu, X., Guo, Y., Maynurdader, 2008b. Preparation of mesoporous polyoxometalate-tantalum pentoxide composite catalyst for efficient esterification of fatty acid. *Catalysis Communications* 9, 1607-1611.
- Zhang, Q., Li, H., Liu, X., Qin, W., Zhang, Y., Xue, W., Yang, S., 2013. Modified Porous Zr-Mo Mixed Oxides as Strong Acid Catalysts for Biodiesel Production. *Energy Technology* 1, 735-742.
- Zhang, S., Zu, Y.-G., Fu, Y.-J., Luo, M., Zhang, D.-Y., Efferth, T., 2010. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. *Bioresource Technology* 101, 931-936.

Table captions

Table 1. Classification and performances of different catalysts used in esterification of different feedstock.

Table 2. Acid loading concentrations and surface area of parent and loaded KIT-6.

Table 3. Percent conversion of FFA to FAME obtained using different catalysts. Experimental conditions were as follows: catalyst to oil weight ratio, 1.5%; MeOH to oil volume ratio, 2:1; temperature, 70°C; reaction time, 3h; Feed, 10g;

Table 4. Biodiesel yield obtained from various feedstock. Experimental conditions were as follows: catalyst to oil weight ratio, 1.5%; MeOH to oil volume ratio, 2:1; temperature, 70°C; reaction time, 3h; Feed, 10g;

Figure captions

Figure 1. SEM images showing the morphology of KIT-6 framework (a) 4.9% STA loaded on KIT-6 (b) 9.5% STA loaded on KIT-6 (c), and 17.4% STA loaded on KIT-6 (d). Scale bar: 10 μm (1a); Scale bar: 5 μm (1b-1d).

Figure 2. N₂ adsorption–desorption isotherms of KIT-6 framework (a), STA exchanged samples (b-e) and unreacted STA control (f). The isotherms suggest that the mesoporosity is preserved after calcination and solid acid exchange.

Figure 3. Pore size distribution KIT-6 silica framework, plotted as pore volume versus pore radius from 2 to 20nm exhibits a narrow peak at ~7.5 nm.

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Figure 5. FTIR spectra of KIT-6 framework, STA exchanged sample STA-D and unreacted STA.

Figure 6. Wide scan XPS spectrum of catalyst STA-D shows the presence of W on the catalyst surface after the acid exchange process.

Figure 7. Representative GC-MS spectra showing the formation of FAMEs upon completion of esterification of various feedstocks: used cooking oil (a), algae oil (b), coffee oil (c), and palmitic acid control (d).

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Table 1. Classification and performances of different catalysts used in esterification of different feedstock.

Catalyst	Feedstock	Important conclusions	Reference
MCM 48 impregnated with 10-40% phosphotungstic acid (PTA)	n/a	It was found that the room temperature synthesis method resulted in catalysts with higher crystallinity, higher surface area and pore volume and were more economical.	(Gucbilmez <i>et al.</i> , 2012)
PTA supported on MCM 41	esterification of acetic acid with n-octanol	MCM 41 could take higher loadings of up to 71% but optimal values were obtained at 60% i.e. surface acidity was maximized at this loading.	(Khder <i>et al.</i> , 2012)
PTA, phosphomolybdic acid (PMoA) and silicotungstic acid (STA) immobilized by sol-gel technique on silica, at 60°C	esterification of palmitic acid with methanol	PTA-silica showed the highest conversion at 100% after a period of 30 h. The catalytic activity was determined as follows: PTA-Si>STA-Si>PMo-Si.	(Caetano <i>et al.</i> , 2008)
PTA, PMo and STA at different loadings from 2.7 wt% to 8.3 wt% anchored to SBA 15	esterification of palmitic acid with methanol at 60 °C	After 6 h of reaction time, it was observed that the conversion of palmitic acid reached 92%, 57% and 45% for the PTA on SBA 15, STA on SBA 15, and PMo on SBA 15 catalysts, respectively; however, STA loaded SBA 15 led to a 80% conversion after a period of 24 h.	(Tropecêlo <i>et al.</i> , 2010)
silicotungstic acid in bulk (STA-A) form as well as silicotungstic acid anchored to silica produced by sol gel method	the esterification of oleic acid with glycerol	STA-A showed higher conversion compared to STA anchored to silica, with conversion of 98% and 96%, respectively, but STA anchored to silica showed a greater selectivity of 95% compared to STA-A which was 89.9%	(Isahak <i>et al.</i> , 2011)

Table 2. Acid loading concentrations and surface area of parent and loaded KIT-6.

Catalyst	Surface area (m ² /g)	% acid exchanged
KIT-6	773.0	0 %
STA-A	551.2	4.9 %
STA-B	491.6	9.5 %
STA-C	413.8	17.4 %
STA-D	350.6	26 %

Table 3. Percent conversion of FFA to FAME obtained using different catalysts. Experimental conditions were as follows: catalyst to oil weight ratio, 1.5%; MeOH to oil volume ratio, 2:1; temperature, 70°C; reaction time, 3h; Feed, 10g;

Catalyst	Conversion in %			
	Algae oil	Coffee oil	UCO	Palmitic acid
KIT-6	2	7	1	1
STA-A	49	60	66	49
STA-B	89	80	84	62
STA-C	96	95	98	97
STA-D	96	96	99	99

Table 4. Biodiesel yield obtained from various feedstock. Experimental conditions were as follows: catalyst to oil weight ratio, 1.5%; MeOH to oil volume ratio, 2:1; temperature, 70°C; reaction time, 3h; Feed, 10g;

Yield in %				
Catalyst	Algae oil	Coffee oil	UCO	Palmitic acid
KIT-6	1	3	2	0
STA-A	12	23	41	28
STA-B	17	42	69	61
STA-C	25	75	86	96
STA-D	28	81	93	100

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(a)

(b)

(c)

(d)

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