1 **Solid-acid Catalyzed Biodiesel Production,**
2 **Part I: Biodiesel Synthesis from Low Quality Feedstock**

3
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10 **Abstract**

11 A series of catalysts containing phosphotungstic acid (PTA) supported on periodic mesoporous
12 silica were prepared and evaluated for the production of biodiesel from used cooking oil. The
13 catalytic and physical properties of the prepared catalysts were investigated. Mesoporous
14 catalyst, KIT-5 (Korea Institute of Technology 5) loaded with 26% PTA showed high activity for
15 single step esterification, resulting in the successful elimination of a second transesterification
16 step. The yield of fatty acid methyl esters was 93% from used (waste) cooking oil and ~100%
17 from pure palmitic acid. In addition, the solid acid catalyst retained a proportion of its original
18 catalytic activity after repeated recycling steps. Thus, the prepared solid acid catalyst has the
19 potential to be used for the production of biodiesel from feedstock that contain high amounts of
20 free fatty acids.

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23 **Keywords:** mesoporous; KIT-5; cooking oil; palmitic acid;
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1. Introduction

Biodiesel forms one of the components of a comprehensive solution to the world's dependency on fossil fuels for transportation (Dovì *et al.*, 2009; Sharma and Singh, 2009). Biodiesel functions in a fashion similar to petroleum diesel (petro-diesel) but results in lower emissions (Wan Ghazali *et al.*, 2015). Just as energy will have to come from various sources in the near future, so should biodiesel feedstock, and hence, the use of a diverse range of agricultural products for production of both fuel and other resources is a welcome approach. Currently, industrial production of biodiesel predominantly utilizes virgin vegetable oil or animal fat feedstock (Kondamudi *et al.*, 2011; Kumar *et al.*, 2011; Leung *et al.*, 2010).

Traditional processes for biodiesel production from oils were typically developed in the early 1940s-50s (Ma and Hanna, 1999). Observations that have been made over the years about the transesterification process include: (i) excess alcohol (greater than 1.6 times the stoichiometric amount) is necessary for the reaction to proceed towards completion (Gerpen, 2005). To make it cost effective, when high FFA feedstocks are used, the reaction could be conducted in two or more steps, where only a part of the alcohol and catalyst are added initially at each step, and the glycerol is separated at the end of every step (Nie *et al.*, 2006), (ii) short or long chained alcohols could be used; examples include methanol, ethanol, propanol, isopropanol, butanol and pentanol (Leung *et al.*, 2010), of which isopropanol is the only branched chain alcohol (Marchetti *et al.*, 2007). (iii) when high amounts of free fatty acids (FFA) are present in the oils or fats, they should be converted to alkyl esters with an acid catalyst. This could be followed by a standard alkali-catalyzed (like KOH or NaOH) transesterification (Meng *et al.*, 2008). Generally, single step transesterification of oils to alkyl esters is kinetically slower than alkali catalyzed reactions (Cho *et al.*; Sakai *et al.*, 2009).

Used cooking oils (UCO) typically contain 2–7% FFA, depending upon their usage and animal fats contain 5% to 30% FFA (Knothe and Steidley, 2009; Zhang *et al.*, 2003). In comparison, non-generic feedstocks have different properties (Ahmed *et al.*, 2014) and low quality feedstocks like trap grease could approach 100% FFA content (Ramos *et al.*, 2009). When the FFA level is greater than 5%, acid catalysts (such as sulfuric acid) could be used to esterify the free fatty acids to esters as shown in the following reaction (Equation 1):

CDAB	Cetyldimethyl(ethyl)ammonium bromide
KIT-5	Korea Institute of Technology 5
MCM	Mobil Composition of Matter No.
PTA	Phosphotungstic acid
SBA-15	Santa Barbara Amorphous 15
UCO	Used Cooking Oil

1 Palm oil, containing 50.8% free fatty acids, esterified to methyl esters using this
2 technique resulted in a yield of 97% but had a residual acid value of about 5% palmitic acid. The
3 incomplete reaction was probably due to formation of water during the reaction or presence of
4 water in the reactant mixture (Zhang and Jiang, 2008).

5 The most common catalysts used for biodiesel production are homogeneous catalysts
6 such as KOH, NaOH, H₂SO₄, HCl and HNO₃ (Leung and Guo, 2006). On the other hand, the
7 approach based on the use of heterogeneous catalysts provides a promising alternate route for
8 low-cost biodiesel production (Di Serio *et al.*, 2007; Nair *et al.*, 2012; Tang *et al.*, 2013). Ali
9 Alsalmeh *et al.* studied the use of heteropoly acids as catalysts for liquid-phase esterification of
10 hexanoic acid (Alsalmeh *et al.*, 2008). Their catalytic activity which was measured by the turn
11 over frequency both in homogeneous and heterogeneous catalyst systems was found to be higher
12 than that of the conventional acid catalysts such as sulfuric acid (Alsalmeh *et al.*, 2008). When
13 solid-acid catalysts replace liquid acids, corrosion and environmental problems linked with the
14 latter can also be avoided and the product purification protocols can be significantly reduced,
15 thereby simplifying biodiesel production and reducing cost.

16 Properties of solid acid catalysts strongly depend upon the nature and concentration of
17 the acids loaded (Singh and Patel, 2014). Catalyst loading could be evaluated by measuring
18 acidity or by determining the concentrations of the elements present in the solid acid loaded. The
19 determination of elemental concentration in catalysts is usually done by inductively coupled
20 plasma (ICP) spectroscopy since it has very low detection limits (ppm to ppb levels), high
21 sensitivity, and reduced matrix effects due to the high temperature of the argon plasma (Lynch,
22 2003). Solid samples have to be digested with concentrated acids or bases and the final solution
23 is homogeneous and not affected by initial sample heterogeneities (López-Suárez *et al.*, 2008).
24 Several studies have previously employed ICP for the determination of the per cent loading of
25 the solid acid loaded with the framework (Tan *et al.*, 2012).

26 This two-part study aims to investigate the use of solid-acid loaded mesoporous silica framework
27 as a catalyst for the production of biodiesel from used cooking oil and to understand the kinetics
28 of the methyl esterification to elucidate a reaction mechanism. Phosphotungstic acid has the
29 strongest Brønsted acidity in the HPAs series and has been used in a wide variety of applications
30 such as oxidation, alkylation, esterification and hydrolysis (Kozhevnikov, 1998). Recently,
31 interesting studies focusing on phosphotungstic acid (PTA) functionalized catalysts have been
32 published that demonstrate the vast potential of PTA in catalysis (Jagadeeswarai *et al.*, 2010;
33 Singh and Patel, 2014).

34 This study (Part-I) reports on the use of a mesoporous organosilica, loaded with varying
35 concentrations of phosphotungstic acid (PTA), for the esterification of palmitic acid (model
36 compound) and high FFA containing used cooking oil. The mesoporous material chosen was
37 KIT-5 (Kleitz *et al.*, 2003). KIT-5 possesses highly ordered cage type mesoporous structure with
38 cubic Fm3m close packed symmetry, high surface area, large cage type tunable pores, and high

specific pore volume. Also, experiments conducted with low FFA containing oils showed that the proposed acid catalyst works effectively with oils containing high FFA.

2. Experimental

2.1 Catalyst preparation

KIT-5 was prepared in the lab using previously established procedure (Kleitz *et al.*, 2003). PTA was loaded on to this framework at various concentrations ranging between 0 wt% to 40 wt%. Supported PTA catalysts were prepared by aqueous incipient wetness impregnation onto mesoporous silica i.e. by suspending a known mass of an aqueous solution of PTA (i.e. “x” g of PTA in 20 mL distilled water) per 1 g of KIT-5 support. This mixture was stirred for 2 h 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. All chemicals were purchased from Sigma Aldrich® and were analytical or better grade.

2.2 Catalyst characterization

The specific surface area was measured using an Autosorb 2010™ gas sorption analyzer based on the nitrogen adsorption/desorption multipoint Brunauer-Emmett-Teller (BET) method. Morphology was characterized using scanning electron microscopy (SEM). SEM images were obtained at 20 kV. Crystalline nature of PTA in the framework was verified using X-ray diffraction (XRD). XRD patterns were obtained using PANalytical X’Pert Pro X-ray diffractometer with Cu K α radiation. The mesoporous nature of the organosilica framework was confirmed using BET adsorption isotherms. Catalyst chemistry was confirmed using Fourier transform infrared (FTIR) spectroscopy. A Perkin Elmer inductively coupled plasma optical emission spectrometer (ICP-OES) was employed for the determination of the concentration of the active element, tungsten. The wavelength used was 207.912 nm and the integration time was 12 s. The catalysts are denoted as PTA-A, PTA-B, PTA-C and PTA-D where A, B, C and D characters represented the various concentrations of PTA loaded on the KIT-5 framework, as explained in Table 1. The W-ion concentration was used to calculate the amount of acid loaded onto the framework. For this purpose, 0.1 g of the PTA-D catalyst was accurately measured and digested with 15 mL of 5M NaOH solution for 4 h. The solution was then diluted to a known volume and was analyzed for tungsten using ICP-OES. The mass of PTA that leaches from the KIT-5 framework material into the reaction mixture was also evaluated using ICP-OES analyses. For this purpose, 1 g of the PTA-D catalyst was mixed with 10 mL of triple distilled water and was refluxed for 3 h. The leachate was then analyzed for tungsten ion concentration.

2.3 Reaction procedure

UCO was obtained from a local restaurant. The first step in the processing of UCO was to remove the insoluble materials, such as meat, fries and particles, using a strainer. Prior to

1 esterification, UCO was heated to 100 °C to lower the water content, if any. Temperature was
2 then maintained at 70 °C. Pure palmitic acid was used as a control. Palmitic acid was allowed to
3 melt and no further processing step was required. Esterification was conducted in a 100 mL
4 round bottom flask equipped with a magnetic stirrer. 1.5 wt% of catalyst was added to 10 g of
5 feedstock. Feedstocks were either UCO or palmitic acid. The oil to alcohol ratio was 1:2 v/v and
6 1:6 v/v for UCO and palmitic acid respectively. A higher amount of alcohol was used to assist
7 with phase miscibility issues when palmitic acid was employed as a feedstock. It is also assumed
8 to drive the reaction towards completion. However, any excess unused MeOH at the end of the
9 reaction was recycled and re-used. At the end of 4 h, the biodiesel was obtained after draining off
10 the glycerol and the excess methanol was recovered using a roto-evaporator. The product was
11 then washed gently with warm water as a purification step.

12 For recycling studies, the reaction was stopped after 4 h and the resulting products were
13 transferred to a separatory funnel. The catalyst was recovered and washed with hexane. It was
14 further dried at 100 °C to remove any water molecules that could affect its catalytic activity. The
15 resulting oil-free spent catalyst powder was then reused as catalyst for a new reaction under the
16 same conditions. Methanol was recovered from the biodiesel product using a rotary evaporator
17 and reused for subsequent experiments. The amount of methanol recovered was close to 5 mL
18 which is a part of the excess MeOH used for driving the reaction forward.

19 **2.4 Analytical methods**

20 The AOCS official method CA 5a-40 (AOCS, 1998) was used to analyze the FFA content of
21 oils. High-performance liquid chromatography (HPLC, Shimadzu LC-10A) equipped with an
22 ultraviolet photometric detector was used for the analysis of the product samples. A C18 Allure
23 column was used for the separation. The mobile phase B was a mixture of isopropanol and
24 hexane in the volumetric ratio of 5:4, and the mobile phase A was 99.9% HPLC grade methanol.
25 The flow rate of the mobile phases was 0.5 mLmin⁻¹, and the column temperature was set at 40
26 °C. The components identified by the HPLC include triglycerides, diglycerides, monoglycerides,
27 methyl esters, and free fatty acids. The identities and relative proportions of fatty acids in the
28 methyl ester product were determined using a Shimadzu gas chromatography–mass spectrometry
29 (GC-MS) QP 2010 using splitless injection. This was equipped with a SHR-5XLB capillary
30 column (25 mm thickness x 30 m length) and had electron ionization detector (70eV) using
31 helium as a reagent gas. A temperature gradient was selected so that the temperature rose from
32 100 °C to 240 °C at the rate of 1.5 °Cmin⁻¹.

33 **3. Results and Discussion**

34 **3.1 Acid exchange and surface area of catalysts**

35 All catalysts used in this study were calcined. Table 1 reports the amount of acid in wt% that was
36 successfully loaded on the framework and the surface area of the PTA-loaded KIT-5 catalyst.
37 Unloaded KIT-5 had the highest surface area at 978 m²g⁻¹. Among the PTA loaded KIT-5

catalysts, the catalyst with the least amount of PTA loading, namely PTA-A (with ~4.1% loading) had the highest surface area due to lesser pore blockage by the loaded phosphotungstic acid. An increase in solid-acid loading is expected to result in lower surface area but also increased yield and conversion.

3.2 FTIR, SEM and XRD analysis

FTIR spectra corresponding to KIT-5 framework, PTA loaded on KIT-5, and framework free PTA is shown in Figure 1. The vibrations of asymmetrical/symmetrical stretching at 1633, 1080 and 816 cm^{-1} corresponds to Si-O-Si bonds (Peña-Alonso *et al.*, 2002). Also the feature at ~949 cm^{-1} relates to Si-OH vibrations of surface silanols which is a typical characteristic of mesoporous silica (Wang *et al.*, 2008). Pure PTA shows the typical IR absorption at approximately 1080 (P-O), 982 (terminal W=O), ~897 (W-O-W) cm^{-1} which are asymmetric vibrations associated with typical Keggin anions (Staiti *et al.*, 1999). A covalent bonding peak was observed at 726 cm^{-1} and is assumed to be a stretching vibration of W-O bonds which is usually observed at 730 cm^{-1} (Hough, 2007). There is a slight shift in the peaks due to the loading of PTA on the framework. The higher activity of PTA supported catalysts compared to plain support could be due to the Lewis acidity arising due to the stronger interactions between PTA and -OH groups of silica.

Also, the presence of PTA on loaded catalysts was confirmed using SEM and XRD. The SEM images shown in Figure 2a, 2b, 2c, 2d corresponding to PTA-A, PTA-B, PTA-C, and PTA-D respectively confirmed the particle size of KIT-5 framework, which is a few μm (Mushrush *et al.*, 1991). The exact particle diameter of PTA is unknown but is estimated to be in the 10-20 nm range. The investigated KIT-5 contains pores with diameters between 2 nm and 34 nm. Mesoporous silica materials consisting of interconnected large pore cage type mesoporous system with three-dimensional porous network are advantageous than those consisting of a hexagonal pore structure with a uni-dimensional array of pores. By controlling particle size, very specific pore characteristics can be designed into a product. Pore characteristics often are the key to catalyst performance. In this case, W ions react with the silica template collapsing/blocking the microporous channels, if any, in the KIT-5 and resulting in the large mesopores and macropores (17 and 50 nm) in the catalyst obtained. These results indicate that PTA molecules were immobilized in the channels of silica and dispersed in a monolayer on the surface.

The powder XRD patterns of pure PTA, mesoporous calcined KIT-5 and PTA supported on KIT-5 are shown in Figure 3. The peaks are clearly resolved and the incorporation of PTA on KIT-5 is evident. XRD spectra confirm the Keggin structure of PTA. Two small broad diffraction peaks: $2\theta = 25.3^\circ$ and 36.6° for Keggin structure corresponding to bulk crystal polytungstate (PW) are observed, which indicates that the intact Keggin structure of PW starts to aggregate on the pore walls of KIT-5. Compared with the other porous silica materials, the large pore sizes and high surface area of KIT-5 would accommodate more discrete heteropoly acids. XRD studies on other silica supported phosphotungstic acid materials produced similar

XRD patterns and confirmed the formation of small crystallites of PTA when higher amounts of acid was loaded and did not show any diffraction peaks with low concentrations of heteropoly acids indicating the well dispersed nature of the heteropoly acid (Bardin and Davis, 2000).

The calcined product was mesoporous and the loaded product retained mesoporosity as indicated by N₂ sorption isotherms. According to the classification of the isotherm types by International Union of Pure and Applied Chemistry, the isotherms obtained from KIT-5 and PTA loaded KIT-5 exhibited mesoporous behavior (Type IV/Type V). Also, the data indicates that the mesoporous property of the parent material is not compromised due to addition of PTA (Figure 4). The isotherm displayed no indication of any changes in the mesostructure related to PTA incorporation indicating that the particles were either too small or well dispersed. These results are indicative of a stronger interaction between PTA and silica.

3.3 Catalyst stability studies

Leaching of active material from a catalyst is undesirable and thus leaching studies were performed to confirm the stability of the catalysts. Analysis results revealed that 0.0045 g of PTA had leached from the catalyst framework; this corresponds to 1.5% of the total mass of PTA (0.3 g) added to the framework. Although PTA is highly soluble in water, results indicate that a large amount of PTA is still retained on the catalyst following leaching studies. This could be due to the W-O covalent bonding observed in the PTA-D catalyst, as discussed in section 3.2. The results obtained from the leaching experiments confirm the stability of the catalysts used in this study.

3.4 Yield and conversion

UCO, canola, and corn oil had a FFA content of 5.94%, 0.15%, and 0.17% as oleic acid, respectively. The corresponding acid numbers were 11.88, 0.30, and 0.34 for UCO, canola, and corn oil, respectively. Palmitic acid was a pure compound, and had a FFA content of 99% and acid number of 197.0. Reactions were conducted under the same operating conditions in order to evaluate the methyl ester yield. The 3/27 test and a pHlip test was used to qualitatively determine if there were large quantities of triglycerides (including mono- and di- glycerides) present in the reaction during the final stages of the process (Burton, 2008; Von Wedel, 2006). A ratio of 9 parts methanol to 1 part biodiesel was used for the 3/27 test. In this study, the mass of the biodiesel was measured when no visible settling of oily material or turbidity was observed.

The yield of biodiesel was determined using the following Equation 2 (Azcan and Danisman, 2007; Schinas *et al.*, 2009):

$$\text{Yield} = \frac{\text{weight of biodiesel}}{\text{weight of feedstock}} \times 100\% \quad \dots(2)$$

In the current work, the use of PTA-D led to a maximum yield of 93% with UCO feedstock and 100% with palmitic acid. The UCO feedstock contains FFA and glycerides when compared to palmitic acid which is a pure model FFA compound. Therefore, MG, DG and TG were also transesterified in addition to esterification of FFA. Thus, the catalytic activity could vary leading to slight differences in yield observed.

The results show that higher acid loadings lead to higher yield. KIT-5 and framework-free PTA were used as controls. KIT-5 framework did not convert FFA's due to its low acidity and ion exchange capability, which limits its effectiveness as a catalyst by itself.

When PTA was loaded, the esterification was effective with yields greater than 90%. When used with low FFA containing oils such as corn oil, the catalyst was inactive. This also proved that the catalyst was effective only with high FFA containing oils owing to its acidic properties.

The percent conversion of FFA to its corresponding fatty acid methyl esters (FAMES) was calculated by Equation 3 (SathyaSelvabala *et al.*, 2011):

$$\text{Conversion} = \frac{\text{acid value}_{\text{initial}} - \text{acid value}_{\text{final}}}{\text{acid value}_{\text{initial}}} \times 100\%$$

...(3)

The maximum conversion of 100% and 83% for palmitic acid and UCO was obtained with PTA-D. The acid value of used cooking oil reduced to 2 mg of KOH⁻¹ after acid esterification from an initial value of 11.88 mg of KOH⁻¹. The percent conversion obtained from all experiments conducted in this study is provided in Figure 5.

In comparison to other studies in the literature, PTA loaded materials were found to be generally more efficient than any other mesoporous catalysts for esterification (Fauzi and Amin, 2013; Olutoye and Hameed, 2011; Zhu *et al.*, 2013). Use of Cs-doped hetero poly tungstates resulted in 100% palmitic acid conversion after 6 h of reaction, with 90% selectivity to the methyl ester and catalysts were recoverable with no leaching of soluble hetero poly tungstates (Narasimharao *et al.*, 2007). Use of 25 wt% PTA/Nb₂O₅ at conditions of 200 °C, 18:1 alcohol to oil molar ratio, and 3 wt% catalyst loading for the transesterification of used cooking oil with high free fatty acids with methanol, resulted in a maximum ester yield of 92 wt%. The catalyst was recycled and reused with negligible loss in activity (Srilatha *et al.*, 2010). 12-tungstophosphoric acid (10-40%) on zeolite H β were synthesized, and 30 % loaded catalyst was used in the esterification of oleic acid with methanol and a 84% conversion was observed (Patel and Narkhede, 2012). MCM-48-supported hetero poly tungstates catalysts were used in the esterification of long-chain fatty acids and alcohols in supercritical CO₂ medium at a temperature of 100 °C and a short reaction period of 6 h (Sakthivel *et al.*, 2008). Heterogenized

heteropolyacids, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ and $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ were shown to catalyze rapeseed oil transesterification with ethanol at 80°C and conversions observed was 27%, 14% and 5% for $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ and $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ respectively (Hamad *et al.*, 2008). In the esterification reaction of *n*-butanol with acetic acid, both chemically and physically immobilized HPW showed similar catalytic activity around 80%. During repeated uses, rapidly decreasing catalytic activity was observed in the case phosphotungstic acid impregnated palygorskite (Zhang *et al.*, 2010). Duan *et al.* synthesized $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on magnetic iron oxide particles, tested them in palmitic acid esterification with methanol and observed a conversion of 90% at 65°C (Duan *et al.*, 2013). CDAB (cetyldimethyl(ethyl)ammonium bromide) and SBA-15 were studied for esterification of oils. SBA-15- SO_3H -P123 was found to be acidic in nature with surface acidity. The biodiesel yield was 85% after 20 h of reaction. CDAB- SO_3H showed a 55% yield under similar experimental conditions (Lin and Radu, 2006). Silica supported phosphoric acid was investigated for biodiesel production from triacetin and the conversion was extremely low at less than 10% (López *et al.*, 2005). MCM-41 was also tested for the transesterification of soybean oil and a yield of 85% was obtained at 60°C using 10 wt% of catalyst for 24 h (Georgogianni *et al.*, 2009).

The above discussed solid acid catalysts when investigated for biodiesel synthesis suffered from limitations such as limited catalyst life, difficulty in recyclability, and/or low yields in comparison with the current synthesized catalyst.

3.5 GC-MS/HPLC Analysis

The GC-MS (gas chromatography–mass spectrometry) was used to analyze the free fatty acids and methyl esters found in the feedstock and products. Spectra indicated that FFAs such as hexanoic acid, decanoic acid, octanoic acid and eicosanoic acid in the feedstock were converted to their corresponding methyl esters. Figures 6a and 6b indicate the complete conversion of palmitic acid and UCO to biodiesel respectively. Figure 6c shows the spectra of low FFA corn oil at the start and end of the esterification reaction. The two spectra are very similar indicating the absence of any catalytic activity when feedstock contains lower amounts of FFA.

Figure 7 shows a direct comparison in the HPLC chromatograms between the feedstock and the methyl ester formed. The consumption of triglycerides and diglycerides to form fatty acid methyl esters is clearly observed.

3.6 Recycling studies

Recycling of the active catalyst is of economic importance for batch processes utilizing catalysts for the production of biodiesel. The main advantage in heterogeneous catalysis is the efficient catalyst recovery. This part of the study shows that this catalyst has been active in the heterogeneous phase, is efficient and can be recovered via a simple recycle protocol. Further, other studies have shown that heteropoly acids anchored to mesoporous supports can be recycled and have been proven to have good recyclability (Ren *et al.*, 2010; Sofia *et al.*, 2009). The

recyclability of WO_3/ZrO_2 was studied under the reaction conditions of 200 °C, 3 wt% catalyst, 5 h and 15:1 methanol to oil molar ratio. The catalyst was recycled without appreciable loss in activity (Sunita *et al.*, 2008). In another study, a small amount of PTA was found to leach from SBA-15 into liquid phase during the esterification of palmitic, stearic and oleic acid with methanol (Tropecêlo *et al.*, 2010). A similar catalyst, SiPW-8, was used in the production of 1,1-diacetates from aldehydes and was successfully recycled for more than 4 cycles with minimal loss in catalytic activity (Wang *et al.*, 2006). Although this is an entirely different application, it helps to signify that these materials are recoverable and recyclable. The result of the four cycle experiment has been summarized in Figure 8. At the end of the fourth cycle, the conversion had decreased to 51% from 83%, falling about 10% with each recycle. These are conservative results which will only improve in practice due to the fact that the starting mass of catalyst is very small in these bench scale experiments and thus the recovery might be affected to a larger extent than when starting with a larger mass of the catalyst. Some losses are expected due to leaching of PTA and slow decrease in active surface area of catalysts due to oil adsorption of some sites. While, the conversion and yield was seen to be lower with each recycle, the recovered catalyst did not show any significant deactivation in comparison with similar catalysts which showed around 27% deactivation in other studies (Sharma *et al.*, 2011) and therefore confirms that these heteropoly acids loaded on high surface area catalysts can be easily recycled for up to 4 cycles. However, recycling efficiency can be improved by using more sophisticated industrial techniques rather than simple laboratory techniques used here. This will also lead to higher conversion after recycling than those reported here. In summary, the most efficient catalyst was PTA-D and important results from the use of that catalyst are summarized in Table 2.

4. Conclusions

Requirements for a good solid acid catalyst for biodiesel synthesis by esterification are (i) high acid concentration to maintain an acceptable reaction rate, (ii) high surface area, and (iii) high conversion and yield. In this study, a mesoporous material based solid acid catalyst, namely PTA loaded KIT-5, was found to satisfy all the above requirements. The highest experimental conversion was 83% for UCO and 100% for palmitic acid at the optimum condition of 4 h reaction time, 2:1 and 6:1 volume ratio of methanol to oil respectively for UCO and palmitic acid, 70 °C reaction temperature, and 26.5 wt% catalyst loading. Catalyst recycling studies indicated that a small amount of acid leached out from the framework leading to a decrease in conversion with each recycle. In conclusion, PTA loaded KIT-5 was synthesized, characterized, and was shown to convert high free fatty acid containing feedstock into biodiesel. The kinetic model for the esterification of UCO to biodiesel was established and will be discussed in part II of this article.

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Table captions

Table 1. Surface area and amount of phosphotungstic acid loaded on to the framework of various catalysts used. KIT-5 refers to framework with no catalyst and catalyst with notations 'PTA' refer to PTA loaded KIT-5. The large specific surface area of the catalyst ensured good contact between the reactant molecules and catalytic active sites.

Table 2. Summary of results obtained from the use of catalyst PTA-D, which was found to be the most effective catalyst in this study.

Figure captions

Figure 1. FTIR Spectra of KIT-5, PTA and PTA loaded on KIT-5. The symmetrical/asymmetrical stretching corresponding to Si-O-Si bonds and Si-OH vibrations of surface silanols that are characteristic of mesoporous silica are shown.

Figure 2. SEM image of (a) PTA-A, (b) PTA-B, (c) PTA-C, (d) PTA-D. The morphology and size of the catalyst particles were as expected. Agglomerations of small spherical particles were observed. There was negligible difference in particle surface morphology between the KIT-5 host and PTA exchanged KIT-5.

Figure 3. XRD patterns of PTA, KIT-5 framework and PTA incorporated KIT-5. Increasing amount of PTA in KIT-5 can be seen to lead to an increase in the intensity of the PTA peaks in the loaded catalysts.

Figure 4. N₂ adsorption/desorption isotherms of (a) KIT-5 (b) PTA-A (c) PTA-B (d) PTA-C (e) PTA-D. KIT-5 and PTA loaded KIT-5 exhibit Type IV/Type V mesoporous behavior, which is typically observed for the mesoporous samples with a cage-type pore structure.

Figure 5. Percent conversion of used cooking oil and palmitic acid to FAME obtained with various catalysts. While use of palmitic acid is seen to result in 100% conversion, use of used cooking oil only leads to a maximum of 83% conversion.

Figure 6 (a) GCMS spectra of UCO prior to and after conversion using PTA-D. All identified components have been labeled. (b) GCMS spectra show methyl ester formation when palmitic acid was used as a feedstock on reaction with PTA-D and PTA; Spectra of pure palmitic acid is provided for comparison. (c) GCMS spectra show that PTA loaded KIT-5 catalyst is unable to convert oils with low FFA.

Figure 7. HPLC system allowed for the detection of mono-, di- and tri-glycerides as well as methyl esters. The difference between the feedstock and the biodiesel is clearly demonstrated in which the feedstock contains more mono-, di- and tri-glycerides and the biodiesel sample contains a small quantity of unreacted tri-glycerides and methyl esters.

Figure 8: Yield and conversion of used cooking oil to biodiesel from recycling studies for each run.

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Desired Catalyst	Amount of acid loaded on framework	Surface area (m ² g ⁻¹)
KIT-5	-	978
PTA-A	4.1 %	574
PTA-B	7.8%	525
PTA-C	10.6%	447
PTA-D	26.5%	425

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Catalyst – PTA-D		
Mass of PTA loaded on KIT-5 framework	26.5 wt%	
Surface Area	425 m ² g ⁻¹	
Yield	Palmitic acid	100%
	UCO	93%
Conversion	Palmitic acid	100%
	UCO	83%
Recyclability	Recycled for 4 cycles with 20% loss in yield and 22% loss in conversion at the end of 4 cycles.

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Step 1

Catalyst

- Silica framework synthesized
- Phosphotungstic acid impregnated on the framework
- Material morphology and chemistry characterization

Step 2

Esterification

- Feedstock: Used cooking oil and Palmitic acid
- >90% conversion achieved

Step 3

Studies

- Catalyst leaching and recycling studies
- Biodiesel quantification and methyl esters analysis