

Transesterification of Waste Cooking Oil in Presence of Crushed Seashell as a Support for Solid Heterogeneous Catalyst

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ABSTRACT

Developing relatively cheap and widely available resources for heterogeneous solid catalyst synthesis is a promising approach for biodiesel fuel industry. Seashell which is essentially calcium carbonate can be used as a basic support for transesterification heterogeneous catalysts. In the present investigation, the alcoholysis of waste frying oil has been carried out using seashell-supported K_3PO_4 as solid catalyst. The rationale for this derives from the fact that waste frying oil contains both long-chain free fatty acids (FFA) and triglycerides (TG) which are catalysed on acid and basic sites respectively. Thus, the K_3PO_4 /seashell catalyst may serve the dual role of promoting both esterification and transesterification reactions. The catalyst was synthesized following a dipping impregnation of pre-crushed and calcined seashell in an aqueous solution of K_3PO_4 . Samples with different percentage loadings of K_3PO_4 (5 to 25 wt%) were prepared. The catalyst samples were characterised (textural and acid-base properties) and biodiesel production activity was evaluated in a slurry reactor. The liquid phase composition in the reactor was determined using gas chromatography-mass spectrometry (GC-MS) analysis. The effects of different process variables; ethanol: oil ratio (3:1-15:1), catalyst concentration ($10-50\text{g/L}$ of mixture oilðanol) on the percentage yield of ethyl ester were assessed.

Reaction data revealed that K_3PO_4 /seashell solid supported heterogeneous catalyst displayed a quite un-common behaviour during the transesterification reaction of waste oils. Although the catalyst showed the occupation of two different active sites namely acid and base, its catalytic activity was found to highly associated to the strength of its basic sites.

Catalyst BET surface area as well as the ratio of basic to acidic site density (BASD) were found to increase with elevating the amount of K_3PO_4 being loaded on calcined shells. Optimal ethyl ester yield was achieved with a catalyst with $W=0.10$ which was found to be quite beneficial achievement in terms of biodiesel economy.

KEYWORDS

potassium phosphate tri-basic, Seashell, transesterification

1. INTRODUCTION

Biodiesel obtained from the alcoholysis of triglycerides and/or free fatty acids found in vegetable oil and animal fats is a promising alternative fuel for medium to large-scale compression ignition engines. This is due to its unique properties including renewability, biodegradability, non-toxicity and higher O_2 content [1]. Generally, biodiesel combustion is similar to petroleum-based diesel in terms of efficiency and post-combustion emissions [2,3,4,5,6]. With its relatively high cetane number, flash point and lubrication properties, biodiesel is a better option for achieving improved longevity of the powerful compression ignition engine [4].

It has been reported that up to 75% of overall biodiesel production cost is due to the feedstock costs [7,8,9]. Thus, the use of waste cooking oil is becoming more attractive for second generation biodiesel synthesis [1, 2, 10]. It has been suggested that biodiesel production costs can be dropped to half price if spent frying oils are used as the principal feed substrate [11]. In Europe, biodiesel demand at about 10 million tons per year may be met from waste cooking oil conversion alone [12]. However, in many developing countries, the associated collection, pre-treatment and storage



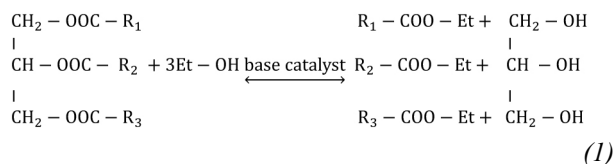
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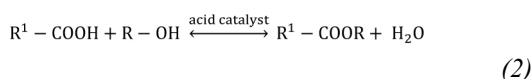
infrastructure for waste oils prior to alcoholysis is lacking and militates against widespread adoption of biodiesel for vehicular applications.

Equations 1 & 2 below illustrate the transesterification and esterification reactions respectively.

Transesterification



Esterification



where R_1 , R_2 , and R_3 refer to the long-chain alkyl groups on the triglyceride molecule while R_{FFA1} and R_{FFA2} are the alkyl groups on the free fatty acid molecule with Et-OH as ethanol. Reactions (1) and (2) are promoted by basic and acidic catalysts respectively.

The catalyst which is normally used in the above indicated reactions are classified as homogeneous (acid or base), heterogeneous (acid or base) and enzymatic (biocatalyst). Based on the type of catalyst being used, the reaction facility and fuel processing units are usually designed and established. Thus evaluating the behaviour of each type of catalyst become essential for the development of biodiesel existed technologies. In spite of their high catalytic activity during the transesterification and or esterification reactions, homogeneous catalysts (acid and base) have displayed many drawback points. These include; their solubility tendencies in the reaction mixture which tends to increase the complexity level of later product purification processes [13,14,15,16,17]. In this sense, implementing the heterogeneous solid catalysts (inorganic and enzyme) for alcoholysis reactions may reduce the overall fuel production costs. This is achieved through the simplification and elimination of biodiesel processing steps as well as its waste treatment stream. Enzyme catalysts appear as an attractive approach for biodiesel synthesis. Biocatalysts are insensitive to the amount of FFA in the feedstock; hence they can simultaneously catalyse both of esterification and transesterification reactions at mild temperatures offering a considerable reduction in energy consumption as well as the reliability on virgin expensive oils for biodiesel synthesis. They are biodegradable and non-corrosive catalysts that would promote a reduction in environmental contamination as well as plant construction costs. Enzymatic catalysed reactions usually require lower amounts of acyl-acceptors namely methanol or ethanol approaching the stoichiometric levels. Also, some types such as immobilized lipase can be reused for many cycles with

high catalytic activity [18]. However, the elevated cost of enzyme catalysts and long reaction periods seem the main obstacles from getting this type of catalyst to be applied in industrial scaled production.

On the other hand, inorganic solid catalysts appear as in hand relatively cheap technique for biodiesel synthesis. These can be classified as acid and basic catalysts. As indicated above, the acid heterogeneous catalysts are insensitive to free fatty acids included in oils. They can simultaneously catalyse esterification and transesterification reactions. Like any heterogeneous catalyst acid solid catalysts can be easily separated from the reaction mixture by simple filtration process. Also, it is quite possible to regenerate and or recycle many types of them. To date, acidic heterogeneous catalysts were extensively investigated from many researchers. A part of those acid zeolites, sulfated zirconia, immobilized sulfonic acids, ion-exchange resins as well as mixed metal oxides [19, 20]. However, problems such as slow reaction rate, high reaction temperatures, the requirements of relatively large quantities of alcohol, and serious corrosion effects are halting the wide utilization of such catalysts in biodiesel industry [21]. It has been stated by Lotero that slow transesterification reaction is originally due to the behaviour of acid catalyst in the reaction mixture [22]. In other words, he stated that as a result of initial protonation reaction of the carboxyl group, the electrophilicity of the adjoining carbon atom would increase which resulted in the formation of an intermediate molecule quite susceptible to nucleophilic attack.

In this sense, basic solid catalyst seems a more promising solution to be implemented in the existed biodiesel industry. This is because basic catalyst offer faster reaction rate than that for acidic one [23]. Unlike acid catalyst, base solid catalysts do not need high reaction temperatures as well as large alcohol quantities. They can be easily separated from the reaction mixture. Some of basic heterogeneous catalysts can be reused and or regenerated. Also, their nature (being base) eliminates the corrosion problems as well as provides a relatively safer working environment. However, the only drawback point with base catalysts (homogeneous or heterogeneous) is that they are quite sensitive to the amounts of free fatty acids and water included in vegetable oil. This becomes a quite problematic issue spatially when low quality feedstock (waste cooking oil) is used [24].

Many types of metal hydroxide, metal oxide, metal complexes and supported catalysts were investigated for biodiesel industry. Their performance during the transesterification reaction were evaluated and reported elsewhere in our previous publication [25]. Some of them have shown an excellent performance during the transesterification reaction [13, 26,27,28,29,30,31,32]. A part of these types is potassium phosphate tri-basic that showed an excellent behaviour during the transesterification reaction of spent frying oil in presence of methanol and or ethanol [33]

[25]. However, drawback points including fouling of organic species and leaching of active metals were clearly noticed [25]. Similarly, calcium oxide (CaO) appears as a promising heterogeneous catalyst during methanolysis conversion of triglycerides to biodiesel. This is mainly due to its high basic strength and relatively cheap resources such as limestone and calcium hydroxide [13, 28]. However, a considerable drop in the percentage yield of methyl ester was observed during the methanolysis of spent cooking oil having 2.6wt% of free fatty acids. Kouzu et al suggested that this reduction in biodiesel yield was mainly due to catalyst decay as a result of strong adsorption of free fatty acids by CaO active sites. It should be mentioned that the use of inert material to produce solid catalyst would enhance its catalytic activity during the transesterification reaction through eliminating the impacts of mass transfer resistance by enlarging the catalyst surface area being available for the reaction to take place [34]. In addition, the availability of relatively cheap and active catalysts is a critical factor for enhancing biodiesel industry. Hence, implementing waste materials to fabricate biodiesel catalysts is a promising approach for boosting its industry via reducing the product final costs [34,35,36,37,38,39,40].

In this sense, activated carbon, eggshell, palm shell, limestone, oyster shell, and fish shell were previously used either as raw material for generating the main active catalysts or as a carrier for other valuable active homogeneous catalysts. Seashell is one of these wastes which are widely available in many countries such as Australia. Seashell is a chemically formative of calcium carbonate CaCO_3 . Thus it seems possible to use seashell as input material for CaO catalyst synthesis after thermally treating it at a relatively elevated temperature 800°C , or as a support for other valuable active homogeneous catalysts without any pre-treatment [35]. It should be mentioned that supporting tri-potassium phosphate on a crushed seashell produced calcium oxide has never addressed in previous contributions. Since then carrying solid catalyst on waste material seems a new approach for modifying the performance of the former catalyst and simultaneously reduce the dependency on valuable support materials such as alumina and silica. Also, fabricating a solid catalyst from two active solid catalysts might be a new approach for eliminating the drawback points of the formers.

Therefore, the present work reports the catalytic activity of tri-potassium phosphate supported by crushed pre-calcined seashell during the ethanolysis reaction of waste cooking oil in a batch scale reactor. Runs were conducted following a standard conventional experimental technique through changing one factor while holding others constant. Examined factors were ethanol: spent oil molar ratio, catalyst percentage loading and catalyst reactor weight, catalyst average particle size. Mixing intensity “stirring speed”, reaction temperature and reaction duration were hold constant

along the experiments at 600r.min^{-1} , 60°C and five hours respectively. The produced catalyst samples were also characterized in terms of their textural and chemical properties. This was achieved through running Nitrogen adsorption-desorption isotherm as well as ammonia and carbon dioxide temperature-programmed desorption TPD tests respectively. In order to get deep understanding for the catalytic behaviour during the transesterification reaction, catalyst characterization results were also correlated with those from the reaction during the course of this work.

2. MATERIALS AND METHODS

2.1. MATERIALS

Tri-potassium phosphate, K_3PO_4 having average particle size (115-150 μm) was supplied by Sigma-Aldrich Pty. Ltd, Australia. A suitable quantity of waste seashell was collected from one of Australian beaches. Waste cooking oil was collected from one of the restaurants on the university campus to be used as the main feedstock for the entire experiments. The collected spent oil was initially a blend of canola and soybean oils (healthy baker blended vegetable oil) which was supplied by (Manildra Group Pty. Ltd, Australia). It should be mentioned that the collected waste oil was vacuumed through 12.5 cm paper filter (542 Hardened Ashless) in order to remove food particles and other impurities. Since then, filtered oil was stored in a highly sealed container and kept in a dark place (chemical liquid cabinet) which is located inside the laboratory in order to avoid the direct exposure to atmospheric air and light and hence oil oxidative stability may be maintained for longer periods [41].

Properties of the employed oil including density, acid value, saponification value, iodine value as well as water content were measured following standard titration methods including ASTM D1959 and D5558 [42]. Based on its saponification, average molecular weight of the oil was calculated [43]. The water content wt% was calculated by using Karl-Fisher auto-titrator (DL31 Mettler-Teledo). Data were reported in previous work [25]. A standard mixture of ethyl esters was supplied by Gayman Chemical Pty Ltd. This standard was used as an internal standard reference for the GC-mass spectroscopy analysis. The mixture included arachidonic, lauric, linoleic, linolenic, myristic, oleic, palmitic, palmitoleic and stearic acid ethyl esters. Ethanol (99.8%) was used as acyl-acceptor for the entire transesterification runs and was obtained from school of chemical science and engineering (UNSW).

2.2. CATALYST PREPARATION

In general, the catalyst was prepared following dipping impregnation technique of crushed pre-calcined seashell in an aqueous solution of active tri-potassium phosphate. Prior the

main impregnation, the collected seashells were washed several times with running water to ensure the removal of any sands and dirt from the surface of the shells. This was followed by another washing with deionised water to neutralize their surface. Drying process was then performed in an oven at 120°C for 12h in presence of ambient air [36, 38]. This was to provide a sufficient time for the evaporation of all water molecules from the shells surface and hence simplify later catalyst processing steps. Also, it is well known that seashells are waste materials with crystalline structure of calcium carbonate mixed with other organic species. In this sense, the presence of such organic species (impurities) may contribute to a significant variation in the catalyst structure during the later calcination step. Thus long drying of the pre-washed shells became more reasonable for water removal as well as combusting other organic species. At this point, the dried seashell was crushed to average particle size $\leq 180\mu\text{m}$. The resulted powder was then calcined in presence of air at 800°C for 4hours in order to convert the inactive calcite calcium carbonate CaCO_3 to a white powder of aragonite CaCO_3 and active calcium oxide CaO [35, 40]. It has been shown that a few minutes of direct contact with atmospheric air was enough to deteriorate the catalyst through the chemisorption of significant amounts of H_2O and CO_2 through hydroxylation and carbonation reactions that yield $\text{Ca}(\text{OH})_2$ and CaCO_3 respectively [44, 45].

However, the catalyst can be re-activated through the evacuation at 550°C and out gassing at 700°C. As indicated above, crushing process was performed before the calcination process in order to avoid re-activation step by eliminating the direct exposure to ambient air that can be occurred during the crashing process. Calcined sample was then stored in a pre-vacuumed desiccator with some pellets of silica gel and KOH. Impregnation was then performed at room temperature with vigorous stirring for 3 hours to give sufficient time for the slow diffusion of active precursors to be absorbed by the pores system of the support (shell). Stirring action was facilitated by using a mechanical stirrer at 3000 r.min^{-1} in a custom made 1L capacity glass reactor. The resulted mixture was then gently dried in an oven at 120°C for 24hours to ensure a uniform distribution of active sites on the surface of the support [46]. This drying process is quite different from the above mentioned drying process. The reason was because this time drying was performed with periodically stirring during the first six hours (critical time) in order to prevent the mixture from quick partial solidification by ensuring a fair suspension of heat through the whole mixture. The resulted solid catalysts were then crushed and sieved to obtain different particle sizes of the final catalyst ranging from 90 to 1000 μm . Catalyst preparation method is summarized in [Appendix \(A\)](#) via [flow chart \(A-1\)](#).

2.3. EXPERIMENTS

2.3.1. Reactor Facility

Transesterification runs were conducted in a 500ml, cylindrical, stainless steel reactor. The reactor was equipped with a high speed (3000 r.min^{-1}) overhead mechanical stirrer (HS-50A). The stirrer has a PL010-40mm, three turbine shape stainless steel blade propeller. The main reactor was essentially submerged in a water bath equipped with an electrical circulating heater to maintain a constant temperature during the reaction period and ensure a homogeneous temperature distribution throughout the bath. Two K-type thermocouples were used to monitor the stability of the reaction temperature. The first one was inserted in the main reactor, while the other in the water bath closes to the external side wall of the main reactor. Thus a quite precise correlation between the reactant temperature and the water bath temperature was obtained which was ($\pm 2.5^\circ\text{C}$).

2.3.2. Transesterification Reaction

Prior each run, 100ml of waste cooking oil was poured in to the reactor. This was followed by the addition of a suitable volume of ethanol alcohol. It should be mentioned that overall mixture (oil and ethanol) was fixed at 200ml at all runs in order to eliminate catalyst suspension issues [25]. Then the mixture of oil and ethanol was stirred gently until the desired mixture temperature was achieved. The reaction is deemed to start when a pre-scaled amount of catalyst is added to the reaction mixture. Sample withdrawing was performed using a syringe through a sampling stainless tube through a special filter in order to prevent the catalyst fine particles from retreating with the withdrawn sample.

By the end of each run which lasted 5hours, 60ml of the reaction mixture was withdrawn and mixed with 10% based on oil weight of pure glycerol. The resulted mixture was then heated using a microwave at 850W for less than minute to accelerate the appearance of two phases. Phase separation was performed using a 100ml separating funnels for around 60 min. Since then around 10ml of the ester was withdrawn from the top layer of the upper phase and neutralized with 0.1MHCL solution (2:1 v/v) and deionised water at (1:1 v/v). The mixture was then centrifuged at 6000 r.min^{-1} for 10min for quick phase separation. Again samples were collected from the top layer and frozen at (0°C) to be ready for GC-Mass analysis. Transesterification reaction is summarized in [Appendix \(A\)](#) via [flow chart \(A-2\)](#).

2.4. ANALYSIS

GC-MS analysis was carried out using HP-6890 gas chromatograph with HP-5973 mass detector (Agilent Technologies, Santa Clara, CA). Chromatographic separation was achieved by a capillary column model SGE 54751 PBX 70 (57m length $\times$ 250 μm diameter $\times$ 0.25 μm film thickness). 20

μl aliquots of each ethyl ester sample were diluted in 10ml n-heptane before GC-MS analysis. Similarly, combined standards (5-500 ppm) of nine fatty acid ethyl esters were prepared in n-heptane. 1 μl of each standard and ethyl ester samples were injected into the column at 250°C on split less mode. Initial oven temperature was set at 130°C which was hold for 5 minutes. This was followed by two stages of temperature ramping of 20°C.min⁻¹ to 210°C and 8°C.min⁻¹ to reach 255°C. This was to allow the resolution of fatty acid ethyl esters. The overall run time was 30.63min. High purity Helium was used as a carrier gas at a flow rate of 53.6 ml.min⁻¹. Electron impact (EI) mass spectra were acquired at an ionizing energy of 70 eV by scanning from 50 to 550 m/z (0.5 s.cycle⁻¹). As indicated above (ref. sub-section 2.1), standards were analysed to determine the retention times and response of individual fatty acid ethyl ester at different concentrations. Plotted calibration curves of fatty acid ethyl esters were used in quantitative analysis. Mass spectra identification of fatty acid ethyl esters in biodiesel samples and standards was performed using Wiley6 library and resulting data was analysed with Agilent Enhanced Chemstation Data Analysis software. The yield of biodiesel was calculated using [equation \(3\)](#) below [26]:

$$\text{Ethyl ester yield EEY}\% = \frac{C_{\text{ester}} \times n}{\rho_{\text{oil}}} \times 100 \quad (3)$$

Where c_{ester} is the mass concentration of ethyl esters in (g.L⁻¹), ρ_{oil} is the oil density in (g.L⁻¹) and n is the diluted multiple of ethyl ester which is the ratio of the total volume of n-heptane internal standard solution to the volume of the ethyl ester sample.

2.5. CATALYST CHARACTERIZATION

Catalyst samples namely K₃PO₄/seashell were analyzed based on their textural properties, type of active sites as well as their concentration on the surface of the support and the strength of these sites. The textural properties of the catalyst including specific surface area and pore size distribution were calculated following a nitrogen adsorption-desorption isotherms at 77 K by Brunauer-Emmet-Teller (BET) from the linear part of nitrogen adsorption isotherm and Barrett, Joyner and Halenda (BJH) methods from the desorption branch of isotherm method (Autosorb-1, Quantachrome instruments). Degassing for the catalyst samples were performed at 573 K for three hours in order to ensure the elimination of any possibly adsorbed moisture from the catalyst porous system.

Temperature-programmed desorption (TPD) of ammonia and carbon dioxide tests were conducted using (Autochem 2910) to obtain active site density and the binding energy with adsorbate gas molecules. Prior each test, catalyst samples

were out-gassed at 150°C for three hours which was followed by flashing with probe gas at 20ml min⁻¹ to ensure the removal of any adsorbed moisture and other volatile species from the porous system of the catalyst. During ammonia NH₃-TPD tests catalyst samples were exposed to 10%NH₃ in nitrogen balance at 70°C for 60min. this was followed by a flow of nitrogen at 20ml min⁻¹ to remove any weakly adsorbed NH₃ for another 60min. then samples temperature was increased from 70 up to 800°C at three ramping rates namely 10, 15 and 20°C min⁻¹. Similarly, the basic properties of the catalysts were also assessed through CO₂-TPD tests. Samples were exposed to 10%CO₂ in Helium balance at 70°C for 60min which was followed by flashing with Helium at 20ml.min⁻¹ ramping rate. Temperature was then increased to 600°C at three different ramping rates namely 20, 25 and 30°C.min⁻¹.

It should be mentioned that all the examined catalyst samples were synthesised following the same technique in terms of stirring intensity, time and drying processes (ref. sub-section 2.2). Also, for comparison purposes only samples with average particle size ranging from 140-250 μm was subjected to the above indicated tests while the similarity in test methods was in highly considered.

3. RESULTS AND DISCUSSION

3.1. CATALYST CHARACTERIZATION

3.1.1. Catalyst Textural Properties

The dependency of specific surface area of calcined seashell on the percentage loading of K₃PO₄ is displayed through [Figure 1](#).

Evidently it seems that pure seashells are non-porous material. This is indicated by its very low surface area as compared to previously recorded material such as $\gamma\text{-Al}_2\text{O}_3$ (BET_{Al₂O₃}=230m².g⁻¹) [47]. This is probably due to chemisorbed CO₂ by the porous system of seashells which did not removed during the pre-treatment (573 K) of the catalyst samples prior BET experiment [44]. Catalyst specific surface area was found to gradually increase with increasing the percentage loading of K₃PO₄. This suggested that the active basic sites provided by K₃PO₄ were actually anchored on the external surface of the support creating what called mono-layer porous system. This was supported by increasing the pore volume with elevated the percentage of K₃PO₄ being added on the shells. This is quite different from what had been reported in previous works using porous γ -alumina as a support for the same active precursors [47]. [Equation \(4\)](#) below illustrates the developments of catalyst BET specific surface area and pore volume which were readily captured by

2 parameters exponential rise with correlation coefficients of 0.96 & 0.99 respectively.

$$T_{\text{prop}} = T_{\text{prop}}^{\text{max}} \left(1 - \exp(-b_{T_{\text{prop}}} W) \right) \quad (4)$$

where T_{prop} represents BET surface area & pore volume, while $T_{\text{prop}}^{\text{max}}$ is BET & pore volume values that corresponding to the optimal percentage loadings of K_3PO_4 on support surface. $b_{T_{\text{prop}}}$ is the K_3PO_4 crystallite formation constant for surface coverage of the support and pore volume blockage constant by K_3PO_4 . W is the percentage loading of K_3PO_4 . Regression of the data in [figure 1](#) to [equation \(4\)](#) gave $T_{\text{prop}}^{\text{max}} = 22.5 \pm 3.3 \text{ m}^2\text{g}^{-1}\text{cat}$ & $8.5 \times 10^{-2} \text{ cc.g}^{-1}$ respectively, $b_{T_{\text{prop}}} = 8.33 \times 10^{-2}$ for BET and 0.25 with catalyst pore volume. It should be mentioned that loading K_3PO_4 on seashells is quite beneficial in elevating the catalyst surface area to be available for the reaction to take place. In virtue, the presence of the majority of active precursor on the external surface of the catalyst pellet would significantly reduce the reaction duration through the elimination of intraparticle diffusion step through the pore system of the catalyst.

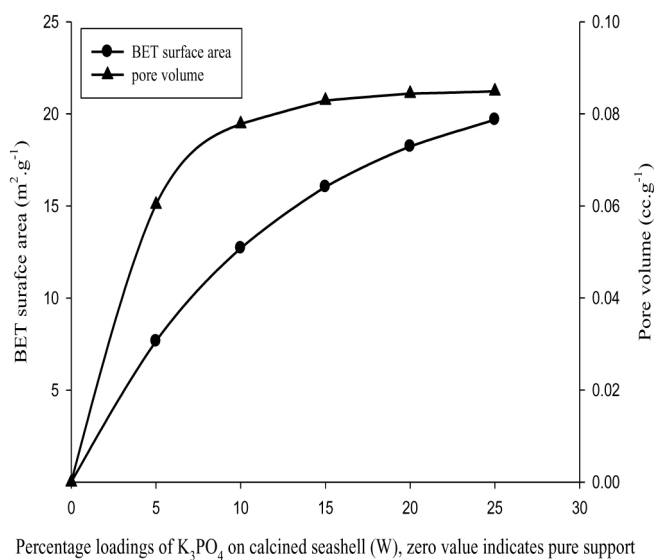


Figure 1. Catalyst surface area versus pore volume at different percentage loadings of K_3PO_4 on calcined seashell

3.1.2. Catalyst Site Density and Strength

It has been observed that catalyst's active site density and strength are playing the most important rules during the heterogeneously catalysed transesterification reaction [48]. In this sense, a temperature-programmed desorption TPD tests were carried out for samples having different percentage

loadings of K_3PO_4 for both acid and basic sites analysis (ref. sub-section 2.5). Ratio of basic to acidic site density (BASD) versus their strength were calculated and plotted against different percentage loadings of K_3PO_4 on seashells via [figure 2](#) below.

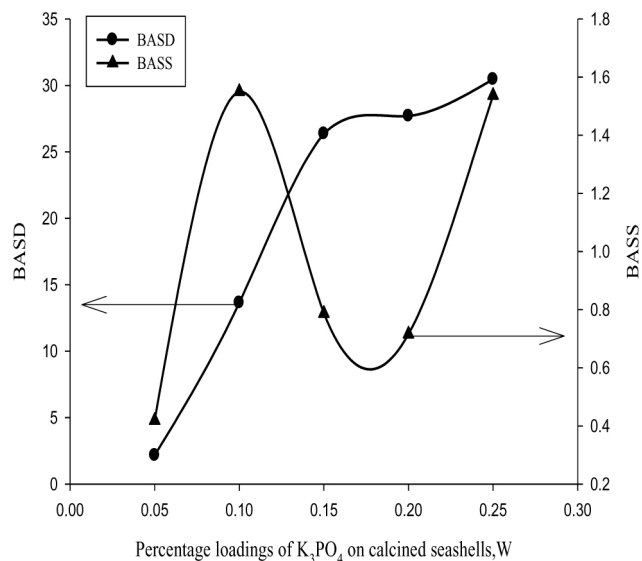


Figure 2. The evolution of BASD versus BASS at different percentage loadings of K_3PO_4 on calcined seashell

It would seem that increasing the percentage loadings of K_3PO_4 increased the basic-acidic site density (BASD) through developing the total number of active basic sites being anchored on the external surface of the shell. However, this development was more pronounced at initial percentages ($0.05 \leq W \leq 0.15$). Beyond medial loading value ($W \geq 0.15$) the growth of BASD was less effective. Thus it can be suggested that at this loading value ($W = 0.15$) almost all the surface of the support was occupied by active basic sites and further increase in K_3PO_4 loadings would not promote significant change in active sites (basic or acidic) concentration. Since then extra basic sites that resulted from further increase in the percentage of K_3PO_4 would anchored on already existed sites. This is also supported by increasing the catalyst mono-layer pore volume with increasing the percentage of K_3PO_4 .

On the other hand, the of basic to acidic site strength (BASS) was found to highly fluctuated with increasing the percentage loading of tri-potassium phosphate (W). Results through [figure 2](#) above, optimal basic-acidic site strength (BASS) was achieved at $W = 0.10$ loading ratio. Thus, catalyst sample with $W = 0.10$ was selected as a representative for TPD results for the all produced catalyst samples. [Figures 3 & 4](#) illustrate both of CO_2 and NH_3 -TPD results of the above indicated catalyst sample.