

Transesterification of Spent Frying Oils over Aluminium Orthophosphate-Potassium Ribbed Bi-Functional Catalyst: Reaction Optimisation Study

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ABSTRACT

This paper reports the optimisation study of a batch scaled ethanolysis conversion of waste frying oil carried out over aluminium phosphate-potassium bi-functional catalysts. All synthesised catalysts were analysed for their structural and surface chemical properties thereby following N_2 adsorption-desorption isotherm and CO_2 and NH_3 -temperature programmed desorption techniques respectively. X-ray diffraction and x-ray photoelectron spectroscopy were also adopted for phase identification and atomic quantification studies respectively. Ethanolysis experiments were carried out eliminating reaction rate limitations caused by solid-liquid interfacial mass transport and intraparticle diffusion. Other operating parameters were also examined in the study. These included; reaction temperature, catalyst percentage loading on support, catalyst weight and reactants molar ratio (β).

Results from the preliminary study revealed that 98.2% ethyl ester yield was achieved over a catalyst sample with highest K_3PO_4 content. Even so, ethanolysis reactions carried out over such catalysts may homogeneously progress due to abnormal increased concentrations of leached K^+ . Homogeneous catalytic behaviour was less pronounced over those with low to medium levels of K_3PO_4 content. The study highlights a catalyst sample with a medium level of K_3PO_4 content as the most heterogeneous catalyst.

Finally, reaction governing parameters were reasonably optimised for a best catalytic performance at conditions of $\beta=12:1$, $SS = 1200r.min^{-1}$, $dp \leq 140\mu m$, $cat = 50g.L^{-1}$ and were found to be optimal. The study identifies aluminium phosphate 15wt% potassium-ribbed catalyst as a quite active bi-functional catalyst for transesterification of spent frying oils.

KEYWORDS: bi-functional catalyst, aluminium phosphate, ethanolysis conversion, spent frying oil

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1. INTRODUCTION

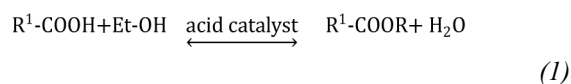
Biodiesel, the mono-alkyl ester of long-chain fatty acids, may be produced via alcoholysis of vegetable oils and animal fats and has been classified as a promising substitute to petrodiesel. It is a renewable, biodegradable, non-toxic, and oxygenated fuel. Biodiesel's comparable technical properties coupled to its superior tailpipe emissions have promoted biodiesel as being a successful alternative to fossil diesel fuel [1]. However, existing biodiesel processing technologies are offering less competitive prices to that of conventional petroleum-based fuel, mainly due to used feedstocks and

production costs. Yet edible vegetable oils (with key ingredients as triglycerides and long-chain free fatty acids, FFA) are commonly utilised along with soluble catalysts in large scale biodiesel practices. Such methodologies usually permit material loss through soap formation (i.e. saponification of the alkali catalyst with the free-fatty acids) and and incorporate an extensive product purification train [2, 3, 4].

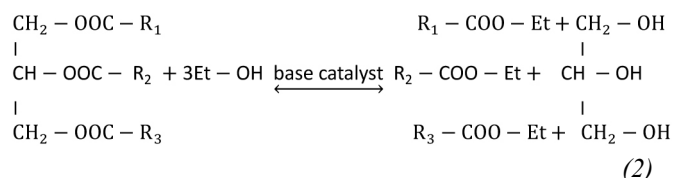
Introducing bioresidues as input feedstocks in the biodiesel industry may promote up to 50% reduction in product processing costs [5]. It is in this respect that spent

cooking vegetable oils become promising alternatives to virgin edible oils. Since waste cooking oils are no longer suitable for human consumption, reprocessing them may add another benefit thereby reducing the environmental impacts of such wastes as well as the reliance on edible fresh oils [6]. Current commercial routes employ sequential esterification of the vegetable oils over acid catalysts followed by triglycerides conversion over basic catalysts as shown via equations 1 and 2 respectively.

Esterification:-



Transesterification:-



where, R_1 , R_2 , and R_3 refer to the long-chain alkyl groups on the triglyceride molecule while R^1 is the alkyl group of the free fatty acid molecule with Et-OH as ethanol. This technique is well suited when low quality feedstocks with relatively high FFA is concerned [7]. The process is quite environmentally sound since it can be performed over the recoverable heterogeneous acid and base catalysts [8]. Even so, the methodology is not recommended from an economic standpoint since it is a time consuming process.

In these aspects, combining both acid and basic within a single processing step through what is called a bi-functional catalyst may become a superior technique to follow. In fact, many kinds of solid acid catalysts have been reported to have the capability to simultaneously catalyse both esterification and transesterification reactions [9]. Since they are solids, they could be easily recovered, regenerated and or recycled for subsequent runs. Examples include zirconia, titania and zeolites. Sulfated zirconia with somewhat higher acid site strength has also shown excellent activity for the methanolysis of palm and coconut oils [10]. In another contribution and in an attempt to improve the acidic feature and mechanical strength of $\text{SO}_4^{2-}/\text{ZrO}_2$, the mixed oxide was combined with alumina and tungsten oxide yielding $(\text{SO}_4^{2-} - \text{ZrO}_2 - \text{Al}_2\text{O}_3)$ and $(\text{WO}_3 - \text{ZrO}_2 - \text{Al}_2\text{O}_3)$ respectively [11]. The resultant catalysts were evaluated in methanolysis of soybean oil at 200-300°C using a fixed bed reactor under atmospheric pressure [11]. Results revealed that $(\text{WO}_3 - \text{ZrO}_2 - \text{Al}_2\text{O}_3)$ catalyst was significantly more active than the counterpart $(\text{SO}_4^{2-}/\text{ZrO}_2)$.

Conversion of about 90% was obtained after about 20 hours at 250 °C over the $(\text{WO}_3 - \text{ZrO}_2 - \text{Al}_2\text{O}_3)$ catalyst. Catalyst stability study also suggested that is a superior candidate with negligible evidence of leaching [12].

Furthermore, sulfated binary oxide $(\text{SO}_4^{2-} - \text{TiO}_2 - \text{SiO}_2)$ exhibited an enhanced activity for biodiesel synthesis compared to the sulfated Titanium oxide $\text{SO}_4^{2-}/\text{TiO}_2$ [13]. This was attributed to increased surface area ($258 \text{ m}^2\text{g}^{-1}$ compared to $99 \text{ m}^2\text{g}^{-1}$). Zeolites, which are essentially solid acids, have also been investigated. They, however, appeared to suffer from intraparticle diffusion problems which was ascribed to their micro-porous structure and surface hydrophobicity [14]. Modification of the cage-like structure to overcome intraparticle diffusion may, nonetheless, be overcome by increasing the Si:Al ratio to enlarge the pore cavities albeit at the expense of a reduction in surface acidity [15].

Nonetheless, drawbacks associated with acid catalysts including slow reaction rate, high reaction temperature are strongly restricting their wide exploitation by the biofuels industry [16, 17, 18]. Lotero et al, 2005 indicated that initial protonation of the carboxyl group is the main root for slow acid-catalysed esterification reactions [19]. This is compared to the alkoxide ion (strong nucleophile) initially created to facilitate a more direct pathway for basic-catalysed transesterification reaction [19]. Besides, spent cooking oil, usually composed of up to 95% triglycerides, may be easily processed over base solid catalysts and/or relatively weak Lewis acid catalysts [20]. Thus, catalysts with dual acid-base sites may become the prime candidates for large scale biodiesel synthesis [4].

Based on the above rationale and for the first time in the current study, aluminum orthophosphate-potassium ribbed bi-functional catalysts were synthesised for the conversion of waste cooking oil with bio-ethanol as acyl-acceptor. The dipping impregnation of $\gamma\text{-Al}_2\text{O}_3$ in an aqueous solution of K_3PO_4 was adopted for catalysts processing. The catalysts were synthesised following five different loading ratios of K_3PO_4 on $\gamma\text{-Al}_2\text{O}_3$ support ranging from 5 to 25wt%. These were characterised by BET surface area and total pore volume, CO_2 and $\text{NH}_3\text{-TPD}$, XRD and XPS. Preliminary ethanolysis reactions were carried out examining the catalytic activity of all produced catalyst samples. Catalyst reusability coupled with K^+ leaching aspects of all used catalysts was already examined and their results were correlated with catalyst loading ratio. The study also extended to optimizing the reaction governing parameters in the presence of a catalyst sample with the most heterogeneous performance.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals, including K_3PO_4 (reagent grade $\geq 98\%$), phenolphthalein, KOH, HCl, $\text{Na}_2\text{S}_2\text{O}_3$, anhydrous Na_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$ were purchased from Sigma-Aldrich Pty. Ltd, Australia. Spent cooking oil (a mixture of canola and soybean oils supplied as healthy baker blended vegetable oil by

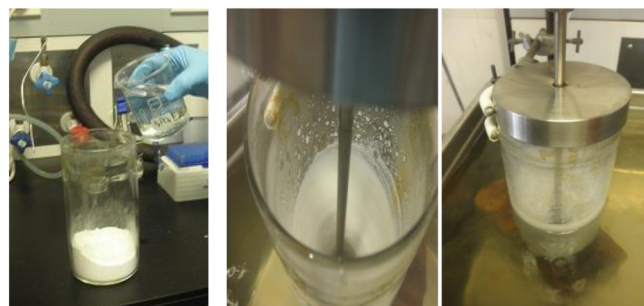
Manildra Group Pty. Ltd, Australia) was collected from one of the restaurants at UNSW. This was filtered to remove food particles and other impurities from the spent oil. The filtered oil was then stored in a sealed container kept in a dark place at 295 K in order to maintain its oxidative stability over a relatively long period [21]. Properties of the used oil including acid value, saponification value, iodine value as well as water content were measured following standard titration methods including ASTM D1959 and D5558 [22]. Based on its saponification and acid values, the molecular weight of the oil was also estimated [23]. Data are shown in Table 1. The used bio-ethanol acyl-acceptor was a 99.8% technical grade obtained from the university chemical store. A standard mixture of arachidonic, lauric, linoleic, linolenic, myristic, oleic, palmitic, palmitoleic and stearic acid ethyl esters was supplied by Gayman Chemicals Pty Ltd. This standard was used as external standard for liquid phase GC-Mass Spectroscopy (GC-MS) analysis of preliminary experiments, [Appendix \(A\)](#)". Similarly, other standards of various concentrations of ethyl oleate ester in n-heptane were prepared and used for product identification and GC calibration of optimisation ethanolysis reactions.

Table 1. Spent cooking oil properties

Acid value mg KOH/100g oil	Saponification Value mg of KOH/g of oil	Iodine Value g iodine/100g of oil	Average molecular mass, g/mol	Water content wt%
1.266	197.26	104	853.34	0.08

2.2. Catalyst preparation

The catalysts were prepared by dipping impregnation method of $\gamma\text{-Al}_2\text{O}_3$ support in pre-concentrated K_3PO_4 aqueous solutions. The used Al_2O_3 support was crushed and sieved to average particle size $dp \leq 180 \mu\text{m}$. This was followed by calcination at 723 K for 12 hours. The procedure involves the formation of a slurry mixture of $\gamma\text{-Al}_2\text{O}_3$ support and K_3PO_4 . The mixture was vigorously agitated in a 2000ml glass reactor using a high speed (13000r.min^{-1}) overhead mechanical stirrer model (HS-50A) for five hours at room temperature as shown in Figure 1. Thereafter, the resultant amorphous gel was gently dried in an oven at 393K for 24 hours [24]. This was followed by solids crushing and sieving to the desired averaged particle size dp . In order to remove soluble ions, the finally obtained catalysts were agitated with deionised water for 5minutes using an ultrasonic cleaner, filtered and dried at 393K for 12hours.



The addition of K_3PO_4 aqueous solution

Stirring at 3000r.min^{-1}

Continuous stirring for up to five hours

Figure 1. Dipping impregnation facility

2.3. Transesterification reactions

2.3.1. Preliminary study "Catalyst screening"

In this part, all ethanolysis runs were carried out by using a 250ml conical flask equipped with a condenser and K-type thermocouple. Heat and agitation intensity were facilitated with the aid of a hot plate magnetic stirrer. Operating parameters were fixed at $\beta = 15:1$ in 50ml overall reaction mixture, $\text{cat} = 50\text{g.L}^{-1}_{\text{solution}}$, $dp = 425\text{-}800\mu\text{m}$, $T = 70 \pm 3^\circ\text{C}$ and runs lasted five hours leaving the catalyst loading $\text{C}_{\text{K}_3\text{PO}_4}$ as a single variable. The procedure involved heating the pre-scaled reactants mixture to the desired reaction temperature. The reaction commenced with the addition of a desired quantity of the catalyst and continued at various agitation speeds for up to five hours.

A 20ml aliquot was withdrawn from the top layer of the resultant mixture and mixed with 10wt% pure glycerin. The mixture was then heated by 850W microwave oven for 30 seconds and left in a separating funnel.

Thereafter, 2ml samples were withdrawn from the top layer of settled mixture, then subjected to a primary leaching test with phenolphthalein indicator. Another 10ml were also collected from the top layer formed in the same separating funnel, washed with warm deionised water (1:1 v/v) and centrifuged at 6000r.min^{-1} for five minutes. Finally, 1ml products were recovered from the centrifuged tubes and frozen for subsequent liquid phase GC-MS analysis.

A quantitative analysis of synthesised fuel samples was carried out by using 6890-HP GC-MS equipped with HP-5973 mass detector (Agilent Technologies, Santa Clara, CA). Chromatographic separation of different fatty acid ethyl esters 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 biodiesel 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. Quantities of 1 μl of each standard and biodiesel samples were injected into the column at 250°C on splitless mode. Initial oven temperature was set

at 130°C and maintained for 5 minutes. The temperature was ramped at 20°C.min⁻¹ to 210°C, then to 255°C at 8°C.min⁻¹ to allow resolution of fatty acid ethyl esters; the overall run time was 30.63 minutes. High purity Helium was used as a carrier gas at a flow of 53.6 ml.min⁻¹. Electron impact (EI) mass spectra were acquired at an ionising energy of 70 eV by scanning from 50 to 550 m/z (0.5 s/cycle). Standards were analysed to determine the retention times and response of individual fatty acid ethyl esters 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 the resultant data was analysed with Agilent Enhanced Chemstation Data Analysis software. The percentage yield of ethyl ester EEY% was given by:

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

where (C_{ester}) is the mass concentration of ethyl esters in g.ml⁻¹, (ρ_{oil}), is the oil density also in g.ml⁻¹ while (n) denotes the dilution multiple of ethyl ester defined as the ratio of the total volume of n-heptane and internal standard solution to the volume of ethyl ester sample [25].

2.3.2. Optimisation ethanolysis reactions study

Ethanolysis runs were carried out by using a custom-made batch-scaled reactor. The reactor is a stainless steel cylindrical shaped having (ID = 70.5mm internal diameter and outer diameter OD=100mm) respectively. A high speed (13000 r.min⁻¹) overhead mechanical stirrer model (HS-50A) was fitted to facilitate the mixing intensity. Condensing of possibly evaporated substrates was facilitated by using a 10mm length, ID = 1mm stainless steel circulating water pipe. The main reactor was essentially immersed in a thermally insulated water bath equipped with an electrical circulating heater (TU1, 1020Watt, Thermoline Scientific Australia) to maintain a constant temperature. Two K-type thermocouples were used to monitor the stability of the reaction temperature. Reaction procedure involved pouring of 200ml of pre-purified waste cooking oil and bio-ethanol at the desired molar ratio into the reactor. The reactor was then placed in the water bath, immediately sealed and the mechanical stirrer fitted in its place. When the desired reaction temperature was achieved, the reaction commenced with the addition of a pre-scaled quantity of catalyst. Precisely 40µl aliquot samples were withdrawn at appropriate intervals and diluted with 1ml of n-heptane for chromatographic analysis.

A 17A-V3 Shimadzu gas chromatograph equipped with a flame ionisation detector (FID) was implemented to monitor the concentration-time profile of ethyl oleate ester. The chromatographic analysis was achieved with MXT-Biodiesel

TG (15m length, 0.32mm ID diameter and 0.1µm film thickness) [26] capillary column. 0.6µl of pre-prepared standards and substrate samples were injected into the column at 1:30 split ratio and 633K. Initial oven temperature was set at 323K and kept for 2.5 minutes. The temperature was then ramped at 15K.min⁻¹ to 473K, from 473 to 493K at 5K.min⁻¹ to 623K at 10K.min⁻¹, from 623 to 653K at 5K.min⁻¹ and held at 653K for three minutes. The overall run time was 38.80 minutes. FID temperature was set at 683K.

2.4. Catalysts characterisation

All synthesised catalysts were analysed in terms of textural properties and surface chemical properties. XRD analyses were also adopted for active phase identification. The textural properties of the catalyst including specific surface area and pore size distribution were calculated following the nitrogen adsorption-desorption isotherms at 77K by Brunauer-Emmet-Teller (BET) from the linear part of the nitrogen adsorption isotherm and Barrett, Joyner and Halenda (BJH) methods from the desorption branch of isotherm method (Autosorb-1, Quantachrome instruments). All solids were degassed at 573K for three hours in order to ensure the elimination of any adsorbed moisture from the catalyst porous system.

Temperature-Programmed Desorption (TPD) of CO₂ and NH₃ were carried out by using a Micrometrics Autochem 2910. The samples were initially out-gassed at 150°C for three hours which was followed by flashing with probe gas at 40ml.min⁻¹ to ensure the removal of any adsorbed moisture and volatile species from the catalyst surface and porous system. Out-gassed samples were then cooled to 70°C at which adsorption takes place. Adsorbate gases 10%CO₂/He and 10%NH₃/N₂ were then admitted at 35ml.min⁻¹ for one hour. This was followed by flashing with carriers He and or N₂ at 40ml.min⁻¹ for another 60 minutes to get rid of any physically adsorbed adsorbate molecules. Desorption then occurred during the catalyst heating at 5°C.min⁻¹ from 70°C to 600 and 800°C as the first temperature ramping for CO₂-TPD and NH₃-TPD tests respectively. After being cooled to 70°C, the adsorption-desorption experiment was then consecutively repeated applying five different temperature ramping rates namely 10, 15, 20, 25 and 30°C. As the site concentration may be calculated based on the largest integrated peak area, the slope from the linear regression of three or more peaks obtained at different ramping rates could be sufficient to estimate the site strength.

The crystalline phases present in all synthesised catalysts were identified thereby using an X-ray diffraction technique. X' pert Pro Multipurpose X-ray Diffraction (MPD) system with Cu K_α radiation ($\lambda = 0.154$ nm) operated at 40 mA and 45 kV was used in the analysis (Figure 3.3), while the X' Pert ScorePlus software was employed to analyse the generated diffractograms.

3. RESULTS AND DISCUSSION

3.1. Preliminary study “Catalyst screening and activity evaluation”

Figure 2 illustrates measured textural properties of all synthesised catalysts with various K_3PO_4 content, $C_{K_3PO_4} = 0 - 25\text{wt}\%$.

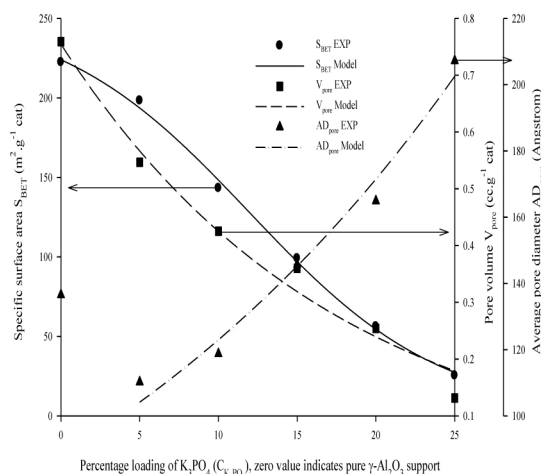


Figure 2. BET specific surface area, pore volume and average pore diameter of $K_3PO_4/\gamma-Al_2O_3$ catalyst samples with different loading ratio

It would seem that increased K_3PO_4 content has blocked the pores of the support promoting a noticeable reduction in the BET area as the K_3PO_4 particles increased in size. The behavior is given by:

$$S_{BET} = \frac{S_{BET}^0}{\left[1 + \exp\left(\frac{C_{K_3PO_4} - C_{K_3PO_4}^0}{b_{BET}}\right) \right]} \quad (4)$$

Where S_{BET}^0 is the specific surface area of unloaded Al_2O_3 support, $C_{K_3PO_4}^0$ is the K_3PO_4 loading corresponding to monolayer coverage on Al_2O_3 at which point the catalyst BET area is about 50% of that from unloaded Al_2O_3 , and $1/b_{BET}$ is the crystallite formation constant of potassium components for pore blockage of Al_2O_3 . Regression of the data from Fig 2 to eq 4 gave $S_{BET}^0 = 256 \pm 12 m^2 \cdot g^{-1} \cdot cat$, $C_{K_3PO_4}^0 = 11.97 \pm 0.77\text{wt}\%$ and $b_{BET} = 6.15 \pm 0.4$ with a correlation coefficient of $R^2 = 0.998$.

Evidently, the exponential drop of total pore volume as K_3PO_4 content increased is given by:

$$V_{pore} = V_{pore}^0 \exp(-aC_{K_3PO_4}) \quad (5)$$

Where V_{pore}^0 is the total pore volume of pure Al_2O_3 estimated as $0.755 \pm 0.03 \text{ cm}^3 \cdot g^{-1} \cdot cat$ and, a is the total pore volume blockage constant computed as $5.7 \times 10^{-2} \pm 4.6 \times 10^{-3}$. Conversely, average pore diameter was reduced at the first dose of K_3PO_4 , $C_{K_3PO_4} = 5\text{wt}\%$ followed by a gradual swell achieving its optimal value at $C_{K_3PO_4} = 25\text{wt}\%$. The reduction is mainly due to the pore blockage by adsorbed ions of K_3PO_4 while the shift to larger average diameters could be attributed to drying effects of amorphous gel mixture that promote the BET area reduction [27].

The bi-functionality of all synthesised solids was evaluated following CO_2 and NH_3 -TPD techniques. The specific base to acid sites density SBASD and strength SBASS were calculated and plotted with respect to different $C_{K_3PO_4}$ in Figure 3 below, while CO_2 and NH_3 -TPD of all examined samples are shown in Appendix B.

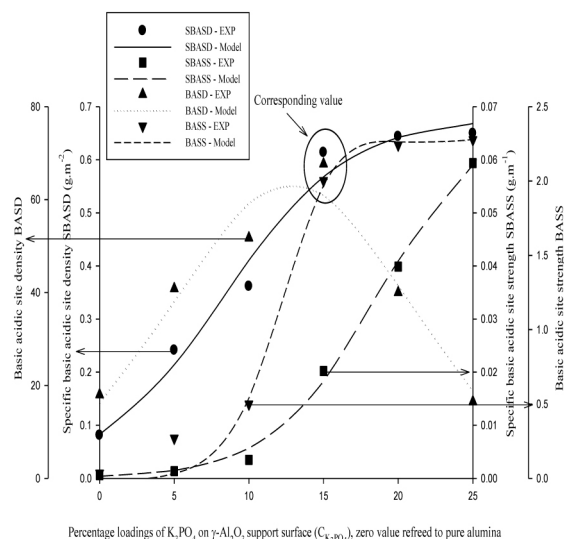


Figure 3. Evolution of SBASD & SBASS against different $C_{K_3PO_4}$

Generally, it would seem that increase in K_3PO_4 content increased both SBASS and SBASD. However, a remarkable drop in catalyst base to acid site density BASD was achieved over $C_{K_3PO_4} \geq 15\text{wt}\%$. This is attributed to increased catalyst acidity mainly due to $AlPO_4$ formed as P:Al molar ratio increased [28]. Since $\gamma-Al_2O_3$ is highly porous, there is always a limit of K_3PO_4 quantity that congregates inside the interlinked pore system. Thus and in this case, it can be suggested that $C_{K_3PO_4} = 15\text{wt}\%$ is the optimal allowable loading ratio at which the resultant catalyst maintained its heterogeneous catalytic behavior. This is in good agreement with results previously observed with carbon supported CaO reported by Tong Wei, 2000 [29]. The BASD trend was normalised through the introduction of S_{BET} term yielding the SBASD. Evidently, no change was observed over catalyst samples having $C_{K_3PO_4} \geq 15\text{wt}\%$. The opposite effect of