Lanthanum phosphate: An efficient catalyst for acrylic acid production through lactic acid dehydration

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Abstract

In this work, biomass-based platform molecule lactic acid conversion to acrylic acid has been studied. A series of Lanthanum phosphate (LaP) catalysts prepared by varying the lanthanum to phosphorus (La/P) mole ratio (i.e. 0.2, 0.35, 0.5, 1.0 and 2.0) and also prepared at different calcination temperatures (i.e. 400, 500, 600 and 800 °C) were investigated. The prepared catalysts were characterised by using different techniques and tested in the dehydration of lactic acid (LA) to acrylic acid (AA) production. All the synthesized catalysts were characterized to understand the physico-chemical properties such as degree of crystallinity, total surface acidity, specific surface area and morphology were analysed. The NH₃-TPD results imply that, all the catalysts exhibited varied amount of total acidity, mostly weak acid sites, with the phosphate loading. The weak acid sites which are mainly Lewis acid sites played an important role in producing AA selectively and efficiently from the LA conversion. The most optimized reaction conditions were determined to obtain highest LA conversion, selectivity, and AA yield. The

catalyst with La/P mole ratio 0.35 and calcined at 500 °C, exhibited best performance with complete LA conversion, AA selectivity of ~74% and a maximum yield of AA~74% was achieved. Furthermore, the LaP(0.35)[500] catalyst was successfully tested for three different time on streams and found to be stable.

1. Introduction

Currently crude oil is being used extensively in producing high performance fuels and chemicals. Today, globally around 70% of crude oil is consumed in producing fuels and 20% is being utilized in producing various chemicals and intermediate compounds [1]. The demand for chemical feedstocks is increasing tremendously with economy in developing countries. The most important global concerns are the climate change and environmental pollution due to fossil-based products. Biomass based refinery and chemicals production can lead to a sustainable society due to its abundance and whole process works under closed carbon cycle. The utilization of lignocellulose as a chemical feedstock found to be an efficient and viable alternative to fossil based raw materials. Moreover, lignocellulose materials are economically and ecologically attractive to produce highly value-added chemicals and intermediates, which are usually produced in low volumes compared to transport fuels [2-4]. Furthermore, it is more advantageous to convert oxygen rich lignocellulosic material to 'drop-in' renewable chemicals that are molecularly identical to conventional petrochemical chemicals. The renewable fuels requires more energy and high operating costs to remove oxygen from the biofuels. The foreseeable future for biorefineries to be economically viable is a challenge in manufacturing high-value chemicals and intermediates, besides low value biofuels [5]. The efficient production of 'drop-in' renewable chemicals can be achieved by using the existing infrastructure and valuechain, thus provide more incentives in terms of energy efficiency with low or zero carbon emissions. In this context, one such chemical produced from biorefinery is the lactic acid, as a platform molecule used in manufacturing of many valuable compounds. Acrylic acid (AA) is considered to be one of the most promising renewable chemicals produced from Lactic acid (LA), because of the bio-based platform molecule and the possibility to produce in large volumes from lignocellulose. Generally, lactic acid (2-hydroxy propionic acid) was derived from the biomass feedstock and LA is an important building block in producing highly valuable chemicals such as AA, acetaldehyde (AD), acetic acid, 1,2-propane-diol, biodegradable poly lactides etc. [6-7] (scheme 1).



Scheme 1. Lactic acid conversion routes to various reaction products.

Lactic acid produced *via* fermentation of sugars such as glucose, starch [8], cellulose [9-10], hemicelluloses [11] and also from glycerol through biochemical processes [12-14]. Among many products produced from the lactic acid conversion, acrylic acid (AA) is one of the important chemicals used in production of polymers. Recently, AA received much attention due to its wide variety of applications such as acrylate polymers (which are used in the manufacturing of paint adhesives, textiles, and leather treating agents) [15-16]. Currently AA is produced industrially by selective catalytic oxidation of propylene in a two-step processes, first step involves propane conversion to propylene, and in the final step, the propylene to AA [17]. Globally, propylene is produced from fossil-based feedstock and thus, contributing to carbon emissions. Henceforth, AA can be produced by using renewable feedstock through gas-phase dehydration of LA, which is an environmentally benign process [18].

Catalytic conversion of LA to AA was studied extensively over different heterogeneous solid catalysts and support materials such as alkali and alkaline earth metal sulphates [19-21], phosphates [22-25], rare earth metal phosphates [26-27], hydroxyapatites [28-31] and various types of alkali and alkaline earth metals modified zeolites [32-37]. Majority of these investigations reported that the dehydration of LA efficiently catalyzed over solid acid-base catalysts, which are typically with different acidity strength such as weak acidic and basic sites [26-29].

Moreover, the catalysts which exhibiting strong acidity strength are favorable in decarbonylation/decarboxylation step to yield acetaldehyde [38-39], which is a major byproduct formation during LA conversion. However, LA conversion over the catalysts with strong basicity produces wide variety of byproducts [32]. Most of the recent studies are focused on using alkali and alkaline earth metal sulphates, phosphates, and zeolites due their desired physico-chemical properties and cost [19-32]. However, there are no studies reported on using rare earth metal phosphates as catalysts. Rare earth metal phosphates have been gaining considerable attention in recent years as catalysts due to their easy preparation, unique properties such as high thermal

stability, melting point, high acidity, and moderate surface area [40-41]. Moreover, metal phosphate catalysts are already employed in various reactions such as alkylation of phenol, dehydration of alcohols, oxidative dehydrogenation, etc. [42-43]. In our previous study, we reported on cerium phosphate catalysts for lactic dehydration reaction and found to be active and selective [26]. In this work we prepared and designed lanthanum phosphate (LaP) based catalysts for the dehydration of LA reaction by varying the La/P mole ratios, which is the novelty of this work.

Recently Guo *et al.* 2016, prepared lanthanum phosphate nano rods using n-butyl amine as a shape directing agent (SDA) for lactic acid dehydration.^[41] The acidity of the catalysts varied due to the molar ratio of SDA to lanthanum, and able to achieve maximum LA conversion of 72% and nearly 50% AA selectivity. In this work, we are able to achieve superior catalytic performance with almost complete LA conversion and better AA selectivity of 74% than Zhen *et al.* 2020. The LaP catalysts are prepared with simple co-precipitation method with varying amounts of lanthanum to phosphorous molar ratio and also studied the effect of calcination temperature.

2. Experimental

2.1 Materials & catalyst synthesis

All reagents are of analytical grade *i.e.* Lanthanum nitrate hexahydrate, ortho phosphoric acid (86% v/v), ammonium hydroxide solution (v/v 25%) and lactic acid are purchased from Sigma USA. The series of LaP catalysts were synthesized based on the method reported by Li et al. [44]. According to the method described in Li *et al.* [44] a series of LaP catalysts (LaNO₃.6H₂O + 86% H₃PO₄) were prepared by precipitation method using 10% aqueous

ammonia as a precipitating agent ($P^{H} \sim 10$). In this work, the catalysts are prepared by varying the La/P mole ratio (*i.e.* 0.2, 0.35, 0.5, 1.0 & 2.0) and then, the catalysts are calcined at different temperatures (*i.e.* 400, 500, 600 & 800 °C). The catalysts are denoted as LaP(m)[T], where 'm' represents La/P mole ratio and 'T' represents calcination temperature. The catalysts containing different mole ratios were prepared by using different amounts of phosphoric acid and keeping La amount constant. Therefore, La/P mole ratios were changed according to the amount of phosphate loadings during the synthesis.

2.2 Materials characterization

All the prepared catalysts were characterized to understand the physico-chemical properties such as phase composition, crystallinity, total acidity, surface area, and morphology using ammonia temperature programmed desorption (NH₃-TPD), N₂ sorption, SEM, XRD, and FTIR techniques respectively.

The powder X-ray diffraction was performed on Ultima IV diffractometer (Rigaku Corporation, Japan) using Ni filtered Cu K α radiation ($\lambda = 1.5406$ A°) operated at 40kV and 30mA. The measurements were recorded at $2\theta = 10^{\circ}-80^{\circ}$ with a scanning rate of 5°/min. The FT-IR spectra of self-supporting disks of powder dispersed in KBr were recorded at room temperature on a Bruker TENSOR 27 spectrometer in the range of 400-3500 cm⁻¹. The specific surface areas were measured by N₂ physisorption at liquid nitrogen temperature over Autosorb-1C instrument (Quantachrome instruments, USA). Prior to the adsorption the samples were degassed under vacuum at 350 °C for 8h and the specific surface area was estimated using multipoint BET method.

The morphological features of samples were obtained by scanning electron microscope (SEM) (Model: EVO 18, Carl Zeiss) device. Prior to SEM analysis, the samples were sprinkled on 1cm stub stacked with a double-sided carbon tape and it was sputter coated in a sputter chamber with gold target to avoid charging and the stub is fixed in the SEM instrument. The elemental composition of the lanthanum phosphate catalysts were determined by Energy Dispersive X-ray spectroscopy (EDS) equipped with SEM instrument (EDS-EVO 18 Oxford instrument), thus, this enables to find the actual metal to phosphorous mole ratio in the sample.

The surface acidity of the catalyst samples were determined by temperature programmed desorption (TPD) analysis using AutoChem 2910 (M/s Micromeritics, USA) instrument with NH₃ as a probe molecule. In a typical experiment, ~ 50 mg dried sample was mounted between quartz wool in a U-shaped quartz tube. The sample was preheated at 300 °C for 1h under high purity He (50 mL/min) flow before adsorption of NH₃/CO₂ at 100 °C for 30min. The physisorbed NH₃ was removed by treating the sample at 100 °C for 30min under He flow (50 mL/min). Finally, the amount of chemically adsorbed NH₃ was estimated using TCD detector by desorbing the probe gas by heating the sample from 100 °C to 700 °C at a heating rate of 10 °C /min under He flow (50 mL/min).

Thermogravimetric analysis (TGA) analysis was conducted by using TA instruments Q500. The sample heated under air at room temperature to 800 °C at a heating rate of 10 °C/min. However, the amount of carbon deposited over the surface of the used catalysts were determined by using CHNS Analyzer-ELEMENTAR Vario microcube model by determining the elemental compositions.

2.3 Catalytic reaction

The prepared catalysts tested in the dehydration of LA under vapor phase conditions at atmospheric pressure. Prior to the reaction, 500 mg of catalyst with mesh size 20-40 mm pellets are diluted with glass beads and packed in the middle section of the reactor (300 mm length and 14 mm inner diameter) using quartz wool. Molecular sieves were placed above the catalyst bed to provide as a pre-heating zone to vaporize the lactic acid feed. About 30 wt.% aqueous lactic acid solution was fed into the pre-heating zone over the catalyst bed using a pump (perfusor FM Infusion by BRAUN, Germany) under nitrogen flow (30 mL/min). The condensed products were collected using ice-trap and then analyzed by GC (Shimadzu GC 2014 equipped with DB-wax column: 30 m × 0.32 mm) connected to flame ionization detector (FID). The condensed products were also analyzed by using GC-MS (HP-5973 quadruple equipped with HP-1MS) with capillary column (15 m × 0.25 mm). The non-condensable tail gases were identified using GC (Shimadzu GC 2014) equipped with molecular sieve-5A packed column (2m × 2mm, mesh-60/80) connected to TCD detector. The LA conversion, products selectivity and yield were calculated by using the following equations (1-3).

3. Results and discussion

3.1 Characterization results

The EDS analysis of the LaP samples presented in the Figure 1, the spectra indicate that the samples containing lanthanum and phosphorous as the major phases. The different La/P mole

ratios were analyzed by EDS analysis and the ratios are presented in Table 1 and results confirmed that the metal content values are well in agreement with the nominal La/P mole ratios. The BET surface areas and textural properties of the catalysts were summarized in the Table S1. The specific surface areas increased slightly from 64.3 m²/g to 71.2 m²/g with La/P mole ratio and then declines (*i.e.* as the phosphate amount increases) from 2.0 to 0.5. Further the surface area decreasing trend was observed in the samples with the La/P mole ratios from 0.35 to 0.2. Moreover, the surface area decreased with the calcination temperature from 500 to 800 °C. The sample calcined at higher temperature (800 °C) is having the lowest surface area of 6.1 m²/g. Generally, calcination treatment decreases the surface area of the samples due to the structural or phase changes occurred during thermal treatment, which can also be observed from the XRD results.



Figure 1. EDS spectra of lanthanum phosphate samples a) LaP(0.35)[500] and b) LaP(1.0)[500]

Catalyst	La/P mole ratio ^a	Total amount of acidity ^b (µmol/g)	Crystallite size ^c (nm)
LaP(2.0)[500]	1.89	321.7	7.9
LaP(1.0)[500]	0.95	369.3	8.5
LaP(0.5)[500]	0.58	409.7	8.6
LaP(0.35)[500]	0.41	494.9	9.8
LaP(0.2)[500]	0.25	576.7	10.4
LaP(0.35)[UC]	0.44	728.6	8.4
LaP(0.35)[400]	0.41	595.5	9.2
LaP(0.35)[600]	0.32	375.7	13.2
LaP(0.35)[800]	0.28	196.6	17.8
LaP(0.35) [500 used]	0.45	481.4	-

Table 1: Catalytic properties of different LaP-based catalysts.

a) Determined from EDS results,

b) Determined from NH3-TPD analysis

c) Calculated from XRD results

The XRD patterns of LaP catalysts are shown in Figure 2. All the samples are showing similar diffraction patterns and the diffraction patterns indicates the rhabdophane lanthanum phosphate crystalline structure (JCPDS file no. 46-1439). The phase transformation from rhabdophane to monoclinic lanthanum phosphate (JCPDS file no. 35-0731) was observed for the LaP(0.35)[T] sample that are calcined at 600 and 800 °C [45]. The shape of the diffraction peaks in the XRD pattern suggests that the samples are highly crystalline and well ordered. However, the LaP catalysts calcined at 800 °C shown better crystallinity with larger crystallite size as

indicated by the sharp and intense XRD peaks [46]. The crystallite sizes of the LaP-based catalysts are calculated by using Scherrer's equation (Table 1).



Figure 2. XRD patterns of a) LaP(m)[500] samples and b) LaP(0.35)[T] samples (where m = mole ratios, T = calcination temperature).

The crystallite size increased gradually with the phosphate amount and the calcination temperature for the LaP(m)[500] and LaP(0.35)[T] catalysts. The LaP(0.35)[600] and LaP(0.35)[800] catalysts shown the large crystallite sizes of 13.2 nm and 17.8 nm, respectively. Whereas, at low La/P ratio and at low calcination temperature, the sample exhibited smaller crystallite size.

The FT-IR spectra of all LaP catalysts are presented in Figure 3. The broad band in the region 3300-3600 cm⁻¹ for LaP samples are attributed to OH stretching vibrations of the residual water and structural hydroxyl (-OH) groups. In addition, the corresponding bending vibration was observed at 1635 cm⁻¹. The intensity of these IR bands declined with lowering the phosphate amount from LaP(0.35)[500] to LaP(2.0)[500] and, completely diminished for the pure La₂O₃ sample (Figure 3a). This phenomenon is also observed with the samples LaP(0.35)[T], which are calcined from 400 to 800 °C. While the predominant peaks between 940-1150 cm⁻¹ are attributed to phosphate P-O stretching, the peaks around 619 and 538 cm⁻¹ corresponds to the O-P=O bending and O-P-O bending vibrations, respectively. The P-O IR stretching band appears to be broad and single for the LaP samples which are calcined at 400 and 500 °C. However, the IR band splitted into two bands for the samples calcined above 500 °C, this indicates the formation of monoclinic lanthanum phosphate phase [45, 47]. The initiation of the monoclinic phase formation above 600 °C is also evident from the X-ray diffraction analysis (Figure 2b).



Figure 3. FT-IR spectra of a) LaP(m)[500] and b) LaP(0.35)[T] catalysts.



Figure 4. SEM images with different magnifications of LaP(0.35)[500]- a) 1 μ m b) 100 nm, LaP(0.35)[UC]- c) 1 μ m d) 100 nm and spent LaP(0.35)[500]- e) 1 μ m f) 100 nm

The Figure 4 represents the SEM images of LaP(0.35)[500], LaP(0.35)[UC] and spent LaP(0.35)[500] catalysts with different magnifications, suggesting that all the LaP catalysts have

a dandelion-like structure without distorting any structure before and after calcination and after reaction. Thus, indicates structure is stable and intact without any phase changes even after repeated thermal cycles. Similar results were reported previously for the lanthanum phosphate-based nano structures [48].

The NH₃-TPD profiles of LaP(m)[500] and LaP(0.35)[T] catalysts were shown in Figure 5. All the peaks observed in Figure 5a and 5b are in the temperature range 100-200 °C, thus, LaP catalysts exhibits mainly the weak acid sites. As the amount of phosphate increases from LaP(2.0)[500] to LaP(0.35)[500] the amount of total acidity increased. Moreover, LaP(0.2)[500] catalyst having the highest phosphate amount among all the catalysts; henceforth, this catalyst also possess moderate and strong acid sites in addition to the weak acid sites. Further, the amount of total acidity decreased with the calcination temperature (see Table 1). This was attributed to the structural and phase changes occurred during calcination.



Figure 5: NH_3 -TPD profiles for a) LaP(m)[500] and b) LaP(0.35)[T] catalysts.

3.2 Catalytic activity

All the prepared catalysts with different mole ratios LaP(m)[500] and calcined LaP(0.35)[T] catalysts are tested in LA dehydration reaction in a fixed bed reactor under atmospheric pressure. The catalyst LaP with 0.35 ratio (calcined at 500°C) found to be most active and selective catalyst and also achieved highest AA yield compared to all catalysts. The LaP(0.35)[500] catalyst possess optimal amount of weak acid sites, probably which are Lewis acidity from P-O bonding and responsible for the superior performance in LA dehydration. Typically, LaP-based catalysts exhibits high Lewis acidity than Bronsted acidity with low basicity [41]. At high La/P ratios, basicity of the samples increases due to increased surface La-OH sites. Moreover, basicity has minimal or no role in catalyzing LA to AA as reported in [41]. Further tests conducted to find the most optimized conditions by changing the reaction parameters over the LaP(0.35)[500] catalyst *i.e.* reaction temperature, feed flow rate (WHSV) and feed concentrations.

Effect of La/P mole ratio

The effect of La/P ratio is an important parameter to optimize and to design a superior catalyst for LA dehydration. The LaP catalyst with 0.35 ratio found to be the most active and selective compared to all tested catalysts. The weak acid sites played an important role in catalyzing the LA to AA and LaP catalyst with 0.35 ratio possess moderately high and optimal amount of acidity, thus exhibited high conversion and selectivity. Initially for 1-2 h, complete LA conversion was achieved and showed a stable trend for the LaP catalyst which is calcined at 500°C. The significant decrease in conversion was observed with time on stream except for LaP(0.35)[500] and LaP(0.2)[500] catalysts. The maximum AA selectivity (> 70%) was

achieved over the LaP(0.35)[500] catalyst but the selectivity declined with mole ratio. The lowest AA selectivity was observed for the catalysts LaP(1.0)[500] and LaP(2.0)[500] compared to all the tested LaP catalysts due to low surface acidity. Henceforth, by varying the La/P ratio can acidity significantly affect the conversion and selectivity due to the changes in the total acidity and the strength. From the literature, it is well known that the catalytic performance of the LA dehydration into AA is mainly depend on the acid-base and redox properties. It is clearly evident that the AA selectivity increased with the phosphate content (i.e. up to La/P ratio of 0.35) and then starts to decrease. The phosphate bonding in LaP catalysts creates weak acid sites with lanthanum. Thus, optimal amount of phosphate *i.e.* La/P ratio of 0.35 exhibited moderately high amount of acidity, which are predominantly weak acid sites corresponds to 100-150°C. Henceforth, the acidity strength of the catalysts played a key role in determining the AA selectivity. However, the samples with low La/P mole ratio (LaP-0.2) possesses highest acidity, but exhibited low AA selectivity. This phenomenon could be explained by the presence of medium and strong acidic sites in the LaP-0.2 sample, which are more favorable in decarbonylation than dehydration mechanism. As a result, the acetaldehyde selectivity found to be the highest for the catalyst LaP-0.2 sample. As mentioned earlier, all the LaP catalysts exhibited highest activity in terms of conversion in the initial hour, the samples with high phosphate content (LaP-0.2 and LaP-0.35) shown stable trend with time on stream. From this result, it is evident that the LA conversion and AA selectivity mainly depends on the total acidity and acidity strength of the catalysts [31]. Hence, the best and optimal ratio of La/P = 0.35 was found to be the most appropriate in gaining the best performance in terms of highest LA conversion, AA selectivity and AA yield due to balanced acidity profile.



Figure 6. Effect of La/P mole ratio for different LaP(m)[500] samples for LA dehydration.
Reaction conditions: LA concentration = 30 wt%, feed flow = 1.5 mL/h, carrier gas (N₂)
= 30 mL/min, reaction temperature = 360 °C, WHSV = 3.156 h⁻¹ and catalyst amount = 500 mg.

Effect of calcination temperature

The influence of different calcination temperatures (T) was studied with LaP (0.35)[T] catalysts (where T = 400-800 °C) on LA conversion, AA selectivity and AA yield, respectively (Figure 7). The catalysts LaP(0.35)[400] and LaP(0.35)[500] showed complete conversion (~100 %) with different AA selectivity values. Over LaP(0.35)[500], a maximum selectivity of ~74% was achieved compared to all catalysts. Even though the LaP(0.35)[400] possess highest acidity than LaP(0.35)[500] but exhibited slightly lower selectivity. The low selectivity is due to the undesirable decarboxylation/decarbonylation of LA to acetaldehyde side reactions. While the LaP(0.35)[T] calcined at 600 and 800 °C shown lower LA conversion and AA selectivity due to low acidity. This result suggests that, acidity not only favors the dehydration but also active in the decarbonylation/decarboxylation side reactions.



Figure 7. Effect of calcination temperatures for different LaP(0.35)[T]. **Reaction conditions:** LA concentration = 30 wt.%, feed flow = 1.5 mL/h, carrier gas (N₂) = 30 mL/min, reaction temperature = 360 °C, WHSV = 3.156 h^{-1} and catalyst amount = 500 mg.

Effect of reaction temperature

The influence of reaction temperature on LA conversion and AA selectivity was tested in the temperature range 300-420 °C and the results were showed in Figure 8. As predicted, temperature had profound effect on conversion and products formation. The LA conversion increased with temperature and reached complete conversion at 360°C, and then conversion maintained stable and constant till 420°C.However, selectivity trend had significant effect due to temperature. Initially, AA selectivity increases with temperature up to 360°C, and thereafter drops to below 30% at 400°C. At higher temperatures, side reactions and byproducts formation rate are favorable compared to desired AA production.



Figure 8: Effect of reaction temperature on LTA reaction over LaP(0.35)[500].

Reaction conditions: reaction feed = 30wt% LA, feed flow rate = 1.5 mL/h, carrier gas (N_2) = 30 mL/min, catalyst LaP(0.35)[500] = 500 mg and WHSV = 3.156 h⁻¹. Others includes 2,3-pentane-dione, hydroxy acetone and some other unidentified products.

Whereas, the reaction temperature had a profound effect on AA selectivity, and it shown a volcano type curve to reach a maximum selectivity of 74% at 360 °C. The major byproduct i.e. acetaldehyde was produced in higher amounts at lower temperature i.e. below 360°C. While other byproduct i.e. propionic acid exhibited low selectivity (below 360°C) and thereafter, acetaldehyde and propionic acid starts to increase and reach maximum at higher temperatures (around 420°C).

Effect of feed flow rates

The effect of feed flow rate i.e. weight hourly space velocity (WHSV) was investigated by using different lactic acid (30 wt. %) flowrates ranging from0.5 mL/h to 2.0mL/h flow rates were studied . A complete LA conversion was achieved until 1.5 mL/h feed flow rate and thereafter conversion decreases steadily due to short reactant residence time. At high flow rates, LA amount will be in higher concentrations compared to the active sites and also shorter reaction times. Further AA selectivity of above ~80% at 0.5 mL/h flow rate was achieved, and thereafter, selectivity slightly drops to 70% at 2.0 mL/h. Overall, a consistent and stable LA conversion was gained for all the flow rates. However, the selectivity fluctuated over the time on stream and a maximum of 75% selectivity was achieved at 0.5 mL/h due to disproportionation side reactions.



Figure 9: Effect of feed flow rates (mL/h): LA conversion () AA selectivity (Δ) and AA yield (\blacksquare). **Reaction conditions:** Reaction feed = 30wt% LA, carrier gas (N₂) = 30 mL/min, reaction temperature = 360 °C and catalyst LaP(0.35)[500] = 500 mg.

Effect of LA concentration

Different lactic acid concentrations were studied and found that the concentration had significant effect on the conversion and selectivity. e A complete LA conversion was achived between 10-30wt.% concentrations and no effect was found. However, at 40 wt.% LA concentration, the conversion gradually drops with time on stream. However, the selectivity varied between 70 to

75 % for 10, 20 and 30 wt% LA concentrations, respectively. As higher the LA concentration, WHSV would be higher according to the given formula. Therefore 30 wt% aqueous LA was used as optimized concentration for 1.5 mL/h feed flow.



Figure 10: Effect of LA concentration (wt%): LA conversion (\circ) AA selectivity (Δ)and AA yield (\blacksquare).

Reaction conditions: LA feed flow = 1.5 mL/h, carrier gas $(N_2) = 30$ mL/min, reaction temperature = 360 °C, WHSV = 3.156 h⁻¹ and catalyst LaP(0.35)[500] = 500 mg.

Stability test

Time on stream (TOS) studies was carried out using LaP(0.35)[500] in an optimized reaction condition. The catalyst was tested for three different thermal cycles without removing from the catalyst bed. In addition, the catalyst was regenerated between each cycle by treating the catalyst bed with air flow (50 mL/min) at 450 °C for 6-8 h in order to remove the coke deposition over the active phase. In the first cycle, a consistent and stable conversion was observed for up to 15 h TOS, and afterward, conversion drops to 80% until 24 h TOS. In the second cycle, a similar trend was observed, starts with complete conversion, and gradually declined after 8 h TOS and reached 80% at 18 h. In the final cycle, starts with complete conversion and rapidly drops to 80% conversion at 12 h TOS. The AA selectivity trend for three cycles found to be similar and the selectivity varied between 70-80%.



Figure 11: Time on stream for three cycles: LA conversion (\circ) AA selectivity (Δ) and AA yield (\blacksquare). **Reaction conditions:** LA concentration = 30 wt.%, feed flow = 1.5 mL/h, carrier gas (N_2) = 30 mL/min, reaction temperature = 360 °C, WHSV = 3.156 h⁻¹ and catalyst LaP(0.35)[500] = 500 mg

3.3 Deactivation studies

The deactivation studies on LaP(0.35)[500] catalyst was performed at different stages of catalytic studies. The deactivation phenomena was thoroughly investigated before and after calcination and after reaction (used catalyst). From XRD (Figure 12), FT-IR (Figure 13) and SEM (Figure 14) analysis was performed and it was confirmed that there are phase and structural

changes have been found for the used catalyst (after reaction). From TGA analysis of the used catalysts exhibited a weight loss peak occurred between 300-450 °C due to deactivation (Figure 14). This weight loss of the catalyst might be due to the carbon gasification over the catalysts as CO_2 . The XRD measurements detected no signal for the carbon deposits on the LaP(0.35)[500] used catalysts (Figure 12), thus confirmed that the formed carbon deposited was presented in the amorphous form. The elemental CHNS analysis also confirmed the presence of carbon formation on the used catalysts (Table 2). The measured H/C ratio on the surface and the bulk of the used catalyst LaP(0.35)[500 used] was found to be lower (H/C = 0.064), which indicates that the formed surface carbon deposits probably presented in the considerable range and much higher on the surface. The Figure 12 represents the NH₃-TPD of LaP(0.35)[500] for calcined and used catalysts.

Catalyst	C%	Н%	N%	S%	H/C ratio
LaP(0.35) [Calcined]	0.11	0.32	0.00	0.00	2.91
LaP(0.35) [Used]	4.07	0.26	0.00	0.00	0.064

Table 2. CHNS analysis for the used and calcined catalysts.

The total surface acidity values for LaP(0.35)[Calcined] and LaP(0.35)[Used] (Table 3.2.1) are quite similar. From Figure 15 it was clearly observed that the weak acidic sites of LaP(0.35)[Used] was decreased. Hence, the additional amount of acidity was given by the peak observed in the moderate acidity range between 300-400 °C, which is attributed to the acidity of

surface adsorbed carbon deposits [49]. Thus, this will affect the conversion and selectivity of the used catalyst.



Figure 12: XRD patterns for calcined and used LaP(0.35)[500]catalysts.



Figure 13: FT-IR spectra for calcined and used LaP(0.35)[500] catalysts.



Figure 14. TGA of Calcined and used LaP(0.35)[500].



Figure 15. NH₃-TPD of Calcined and used LaP(0.35)[500].

4. Conclusion

A low cost and highly efficient LaP based catalysts were prepared with different La/P mole ratios and tested in LA conversion. The total acidity depends on the phosphate loadings in LaP catalysts and highest acidity was found with the high P content sample. The weak acid sites are important in catalyzing the LA dehydration to AA. Further, not only the lanthanum-phosphorous mole ratio influenced the reaction, but also calcination temperature had significant effect on AA selectivity and LA conversion. The correlation between total acidity and activity were exhibited similar trend. The optimized reaction conditions were determined and also deactivation phenomena were thoroughly studied. The LaP catalyst with La/P mole ratio of 0.35 and calcined at 500 °C (LaP(0.35)[500]) shown superior catalytic performance with complete LA conversion and achieved highest ~74% AA yield and selectivity compared to all catalysts. Catalyst deactivation occurred due to the formation of carbon/carbonaceous deposits, but regeneration gained complete activity of the LaP catalysts.

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Contributions

Kanokphorn Sangkharak designed the experiment, conducted research work, compiled data and wrote the manuscript. Kamolphan Chookun conducted research work pertaining to bioethanol, Jutamas Numreung conducted research work pertaining to biodiesel, and Poonsuk Prasertsan is mentor.

conception or design of the work; or the acquisition, analysis, or interpretation of data; or the creation of new software used in the work;

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