Summary and Conclusions

This thesis describes the preparation, characterization and catalytic evaluation of cerium, lanthanum and magnesium phosphates for the vapor phase catalytic dehydration of lactic acid to produce acrylic acid.

Several catalysts containing tungsten oxide supported on Y-zeolites with different SiO_2/Al_2O_3 ratio, mordenite and different metal oxides supported on Y-zeolite (CBV-760) have also been synthesized for the vapor phase catalytic esterification of lactic acid with butanol to produce butyl lactate.

- Chapter 1, gives the general introduction about the solid acid catalysts (metal phosphates and zeolite supported tungsten oxide catalysts) and an up-to-date literature survey on the applications and characterization of metal phosphates and zeolite supported metal oxide catalysts for various techniques have been provided. Importance of renewable source as an alternative to fossil fuels, biomass utilization, lactic acid and acrylic acid production and valorization of lactic acid to value added chemicals also briefly discussed. Finally, the aim of the thesis is given to check the catalytic performance of dehydration of lactic acid to acrylic acid and esterification of lactic acid to butyl lactate in the vapor phase conditioned fixed bed reactor over solid acid catalysts.

- In chapter 2, a brief description of experimental techniques is given viz., the preparation of various metal phosphates and zeolite supported metal oxide catalysts and their characterization techniques like X-ray diffraction analysis (XRD), Fourier

transform infrared spectroscopy (FT-IR), Temperature programmed desorption (TPD) of ammonia, BET surface area, pore size distribution measurements, scanning electron microscope (SEM), EDAX, and Thermo gravimetric analysis (TGA). This section also consists of the flow diagram of catalytic experiments for the valorization of lactic acid to value added chemicals.

- Section A of chapter 3, describes a series of cerium phosphate (CeP) catalysts synthesized by using a precipitation method with varying Ce/P mole ratio ranging from 0.5-3.0. The formation of cerium phosphate was confirmed by XRD and FT-IR techniques. The catalysts were further characterized to understand the morphology and surface area by using transmission electron microscopy (TEM) and N_2-sorption measurements. The acidic and basic sites were measured by CO_2-TPD, NH_3-TPD and ex-situ pyridine FT-IR methods. The CeP catalysts were employed for the dehydration of lactic acid (LA) to acrylic acid (AA) under vapour phase reaction conditions. Among the catalysts examined, CeP catalyst with Ce/P mole ratio 2.5 (CeP(2.5)) was found to exhibit better catalytic performance with conversion of lactic acid ~100 % and 64 % selectivity towards acrylic acid at optimized reaction conditions. The catalytic performance depends strongly on the ratio of acidic/basic sites on the catalyst surface. AA selectivity was found to be highest at acid-base balance factor = 0.56. Time on stream experiments suggest that CeP(2.5) catalyst exhibited constant activity until 20 h after which a slight drop in conversion of lactic acid was noticed. The characterization studies of the spent catalysts using thermo gravimetric (TG), CHNS

and FT-IR analyses suggests the presence of carbonaceous species over the catalyst surface causing deactivation of the catalyst.

- Section B of chapter 3, describes the synthesis and catalytic activity of a series of lanthanum phosphate (LaP) catalysts of varying La/P mole ratio (2.0, 1.0, 0.5, 0.35 & 0.2) with different calcination temperatures (400, 500, 600 & 800 ^{o}C) for the dehydration of lactic acid (LA) to acrylic acid (AA). All the synthesized catalysts have been characterized to understand the physico-chemical properties like crystallinity, surface acidity, specific surface area and morphology. The NH_3-TPD results suggest that all the catalysts consists weak acidic sites and the amount of acidity have been varied with the amount of phosphate loading. After the modification of lanthanum phosphate catalysts with suitable surface acidity (La/P mole ratio) can efficiently dehydrate the LA to produce AA. Not only has the metal-phosphorous mole ratio, calcination temperature also played a major role in AA selectivity and LA conversion. The catalytic performance is shown to correlate with the amount of total acidic sites present on the catalyst surface. Under the optimized reaction conditions (360 ºC, 30 wt % LA flow rate = 1.5 mL/h, WHSV = 3.156 h^{-1}), the LaP catalyst with La/P mole ratio = 0.35, calcined at 500 ºC (LaP(0.35)[500]) was showed the better catalytic performance (~74 % AA yield) compared to other LaP catalysts prepared. Furthermore, the LaP(0.35)[500] catalyst was efficiently tested for three cycles with different time on steams and noticed a marginal drop in conversion up to 80 %. The deactivation studies revealed that the drop in conversion was caused by the deposition

of carbon/carbonaceous species on the catalyst surface but switch to the in situ air flow at 450 ºC could regenerate the LaP catalysts for the LTA reaction.

- Section C of chapter 3, describes a series of MgHP catalysts with different magnesium to phosphorous (Mg/P) mole ratio (2.0, 1.5, 1.0, 0.5, 0.35 & 0.2) at different calcination temperatures (400, 500, 600 & 800 ^{o}C) have been synthesized by using simple co-precipitation method. The physico-chemical properties of MgHP catalysts have been characterized by using various spectroscopic and adsorption techniques such as XRD, FT-IR, SEM-EDX, NH_3-TPD, N_2-physisorption, etc. Magnesium hydrogen phosphates (MgHP) have been set up to be highly effective and stable catalysts for acrylic acid production from lactic acid. The Mg/P mole ratio and calcination temperature were played a major key role in producing the high yield of AA. The Mg/P mole ratio affects the total amount of acidity which is a main determining factor for LTA reaction. The increase in calcination temperature affects the structure of magnesium hydrogen phosphate to form magnesium pyrophosphates which are inefficient to the LTA reaction. Under the optimized reaction conditions (360 ºC, 20 wt % LA feed flow rate = 1.5 mL/h), the MgHP catalyst with Mg/P mole ratio = 0.5, calcined at 500 ºC (MgHP(0.35)[500]) was showed the better catalytic performance (~82 % AA yield) compared to other MgHP catalysts prepared. The catalyst was tested for three cycles of 24 h each and observed that consistent acrylic acid selectivity with only a little drop in lactic acid conversion. Though magnesium hydrogen phosphate catalysts were also suffered with little deactivation but

comparable to the other catalysts studied in this reaction these catalysts are very less efficiently adsorbed the carbon/carbonaceous particles onto their surface.

- Section A of chapter 4, describes the vapour phase esterification of lactic acid with butanol carried out over tungsten oxide supported on Y-zeolite catalysts. The degree of esterification depends on the type of zeolite with different SiO_2/Al_2O_3 ratio, the amount of WO_3 deposited and the total amount acidity produced by the catalyst. There are two series of WO_3 supported zeolite catalysts have been prepared. One is 10 wt % WO_3 supported on Y-zeolites and mordenite namely 10W-400, 10W-720, 10W-760 and 10W-20A having different SiO_2/Al_2O_3 ratio = 5.1, 30, 60 and 20 respectively. The second series is having various loadings of WO_3 (5, 10, 15 and 20 wt %) supported on to CBV-760 (SiO_2/Al_2O_3 ratio = 60) namely 5W-760, 10W-760, 15W-760 and 20W-760. High dispersion of WO_3 species on Y-zeolite was achieved, but at higher loading micro crystallites of WO_3 was detected. Tungsten oxide species were deposited preferentially inside the zeolite structure and interacted with the Brønsted sites as well as on silanol surface groups with the formation of small aggregates. As seen by the differences in conversion over different zeolites, CBV-760 (with SiO_2/Al_2O_3 ratio = 60) and 10 wt % WO_3 supported on it was favored the highest lactic acid conversion and butyl lactate selectivity. Under the optimized reaction conditions (175 ºC, 1:3 LA-BtOH feed flow rate = 1.0 mL/h), the 10W-760 catalyst produced an overall yield of 67 % (80 % conversion and 84 % selectivity) towards butyl lactate. The better performance of the 10W-760 sample was attributed to a better distribution of strength of the acidic sites towards the selective esterification of lactic acid with butanol.

- Section B of chapter 4, describes the vapour phase esterification of lactic acid with butanol carried out over different metal oxides supported on Y-zeolite (CBV-760). A series of metal oxide supported zeolite catalysts (10 wt % of WO_3, MoO_3, Nb_2O_5, V_2O_5 and SnO_2 supported on CBV-760) have been synthesized and employed for the esterification of lactic acid (LA) with butanol to produce butyl lactate. All the synthesized catalysts have been characterized to understand the physico-chemical properties like crystallinity, surface acidity, specific surface area and morphology. The NH_3-TPD results suggest that impregnation of the metal oxides on the Y-zeolite (CBV-760) catalysts enhances the total amount of surface acidic sites relative to that of pure Y-zeolite (CBV-760). The degree of esterification depends on the type of metal oxide deposited and the total amount acidity produced by the catalyst. Among the 10 wt % of WO_3, MoO_3, Nb_2O_5, V_2O_5 and SnO_2 supported on CBV-760 catalysts 10Sn-760 is favoring the highest lactic acid conversion with butyl lactate yield. Under the optimized reaction conditions (175 ºC, 1:3 LA-BtOH feed flow rate = 1.0 mL/h) 10Sn-760 catalyst calcined at 550 ºC exhibited a maximum yield of butyl lactate ~85 % (LA conversion ~95 % and butyl lactate selectivity ~90 %).

- Finally, chapter 5 summarizes the summary and the conclusions drawn from this thesis work.

The most important conclusions that can be drawn from the present thesis are:

1. The CeP, LaP and MgHP catalysts have been prepared by the co-precipation method using the metal nitrate precursor and ortho phosphoric acid using aqueous ammonia as the precipitating agent.
2. The CeP, LaP and MgHP catalysts have been prepared by varying the metal to phosphorous mole ratios (M/P) to get different structural acid properties and with different calcination temperatures to vary the structure of the metal phosphate.
3. These catalysts were employed for the vapour phase dehydration of lactic acid to produce acrylic acid.
4. The physico-chemical characteristic properties of these metal phosphate catalysts have been determined by various spectroscopic and adsorption techniques.
5. The formation of cerium phosphate was confirmed by X-ray diffraction and FT-IR techniques. TEM results clearly suggest that the formation of rod shaped like particles of single crystal.
6. The catalytic performance CeP catalyst strongly depends on the ratio of acidic/basic sites on the catalyst surface. The density of surface acidic sites (surface acidity) and basic sites (surface basicity), which are obtained by normalizing to the sample surface area and measured from the NH_3- and CO_2-TPD peaks. Furthermore, the acid-base balance (acid to base atomic balance) was calculated by the ratio of total amount of acidity to total amount of basicity. AA selectivity was found to be highest at acid-base balance factor = 0.56.

7. The XRD patterns of LaP catalysts resembles to rhabdophane lanthanum phosphate crystalline structure with phase transformation from rhabdophane to monoclinic lanthanum phosphate observed for LaP(0.35)[600] and LaP(0.35)[800] samples.
8. The SEM images of LaP(0.35)[500], LaP(0.35)[UC] and LaP(0.35)[used] with different magnification suggesting all the LaP catalysts have a dandelion-like structure without disturbing any structure difference between the samples before calcination, after calcination and after the reaction.
9. The catalytic performance of LaP catalysts was shown to correlate with the amount of total acidic sites present on the catalyst surface determined from NH_3-TPD measurements.
10. The formation of carbon / carbonaceous deposits on the LaP catalyst surface causes little deactivation in the LA conversion but switch to the in situ air flow at 450 ºC could regenerate the LaP catalysts for the LTA reaction.
11. The morphological features of the MgHP catalysts were assessed by SEM and depicted the flakes like morphology. Interestingly, the calcined (MgHP(0.5)[500]) and the used catalyst (MgHP(0.5)[Used]) samples also show a clear existence of flakes like morphology.
12. Though MgHP catalysts were also suffered with little deactivation but comparable to the other catalysts studied in this reaction these catalysts are very less efficiently adsorbed the carbon / carbonaceous particles onto their surface.
13. Among the three series of metal phosphates (CeP, LaP and MgHP) the MgHP catalysts showed the better catalytic performance towards the acrylic acid production. The order of performance of various catalysts is as follows CeP < LaP < MgHP.

14. Three series of zeolite supported metal oxide catalysts have been prepared to perform the esterification of lactic acid in vapour phase conditions.
15. First series is 10 wt % WO_3 supported on Y-zeolites and mordenite namely 10W-400, 10W-720, 10W-760 and 10W-20A having different SiO_2/Al_2O_3 ratio = 5.1, 30, 60 and 20 respectively. The second series is having different weights of WO_3 (5, 10, 15 and 20 wt %) supported on to CBV-760 (SiO_2/Al_2O_3 ratio = 60) namely 5W-760, 10W-760, 15W-760 and 20W-760. The third series is different metal oxide (10 wt % of WO_3, MoO_3, Nb_2O_5, V_2O_5 and SnO_2) supported Y-zeolite (CBV-760) catalysts.
16. High dispersion of WO_3 species on Y-zeolite was achieved, but at higher loading microcrystalites of WO_3 was detected. Tungsten species were deposited preferentially inside the zeolite structure.
17. The better performance of the 10 WO_3/Y-zeolite (CBV-760) sample was attributed to a better distribution of strength of the acidic sites towards the selective esterification of lactic acid with butanol.
18. The degree of esterification depends on the type of metal oxide deposited and the total amount acidity produced by the catalyst. Among the 10 wt % of WO_3, MoO_3, Nb_2O_5, V_2O_5 and SnO_2 supported on CBV-760 catalysts 10Sn-760 is favoring the highest lactic acid conversion with butyl lactate yield.
19. The NH_3-TPD results suggest that impregnation of the metal oxides on the Y-zeolite (CBV-760) catalysts enhances the total amount of surface acidic sites relative to that of pure Y-zeolite (CBV-760) which enhances the degree of esterification of lactic acid to produce butyl lactate.