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Dehydration of lactic acid to acrylic acid over lanthanum phosphate catalysts: the role of Lewis acid sites[†]

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Lanthanum phosphate (LaP) nano-rods were synthesized using *n*-butylamine as a shape-directing agent (SDA). The resulting catalysts were applied in the dehydration of lactic acid to acrylic acid. Aiming to understand the nature of the active sites, the chemical and physical properties of LaP materials were studied using a variety of characterization techniques. This study showed that the SDA not only affected the porosity of the LaP materials but also modified the acid-base properties. Clearly, the modification of the acid-base properties played a more critical role in determining the catalytic performance than porosity. An optimized catalytic performance was obtained on the LaP catalyst with a higher concentration of Lewis acid sites. Basic sites showed negative effects on the stability of the catalysts. Good stability was achieved when the catalyst was prepared using the appropriate SDA/La ratio.

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1. Introduction

Increasing environmental concerns not only raise challenges but also provide opportunities for the conventional chemical industry. Replacing fossil fuels with renewable feedstock is one of the best solutions to mitigate those concerns. In line with this, transformation of biomass to value-added chemicals has attracted significant attention in recent years. As renewable feedstock, biomass derived materials, mainly cellulose and lignocellulose, have been converted to platform chemicals such as furfural, 5-hydroxymethylfurfural (HMF), levulinic acid, and lactic acid, among others.¹⁻⁴ These platform chemicals can be further upgraded to fuels, high value chemicals, monomers and polymers.^{3,4} Thus, the future chemical industry can be released from the full dependence on fossil fuels. One good example is the production of acrylic acid (AA), one of the important commodity chemicals with an estimated annual production capacity of 4 200 000 metric tons.¹ AA and its alkyl esters are of great industrial importance in the production of polyacrylic esters, super-absorbent materials, washing reagents, paints, and adhesives.^{1,5} Currently AA is manufactured through two-step oxidation of propylene, which is a nonrenewable petrochemical.¹ Recently, tremendous efforts have been devoted to the production of AA from renewable bio-resources, e.g. catalytic dehydration of lactic acid (LA).⁶⁻¹⁰ LA is obtained from the fermentation of biomass and is becoming increasingly available in commercial quantities at low cost.^{1,11}

The catalytic dehydration of LA to AA has been studied using both homogeneous and heterogeneous catalysts. With Na₂HPO₄ and/or NaOH as homogenous catalysts, a yield of AA as high as 58% was reported.¹² But the drawbacks of homogeneous catalysts are their unfeasible separation and recovery. Therefore, significant efforts were devoted to the development of heterogeneous catalysts. The most frequently used heterogeneous catalysts are modified zeolites,^{6,8,10,13,14} sulfates^{5,15} and phosphates.^{7,9,16,17} Sodium Y zeolites (NaY) have been modified by alkali metals,¹⁰ alkaline earth metals¹³ and rare earth metals⁸ to improve the selectivity towards AA. 67.9% selectivity toward AA was achieved on potassium iodide modified NaY zeolites (KI/NaY).¹⁰ In addition, the stability of NaY zeolites was improved by using Na₂HPO₄ as a modifier.⁶ 77% selectivity toward AA was reported using alkali metal modified ZSM-5 zeolites.18 BaSO₄ showed an efficient activity for the dehydration of LA. 74% selectivity towards AA was obtained under optimal conditions.¹⁵ CaSO₄ doped with phosphates gave 63.7% yield.⁵ Most recently, high selectivity toward AA (87.0%) has been reported by Matsuura et al., using hydroxyapatite catalysts.¹⁹ The deactivation mechanism of zeolite based catalysts was studied by Näfe et al. They suggested that the deactivation was caused by the deposition of species containing carboxyl groups on the catalysts.²⁰

The catalytic mechanism of LA dehydration has been extensively studied. It is believed that the acid–base properties of the catalyst play an essential role in the selectivity toward AA. It has been proposed that Brønsted acid sites catalyze the decarbonylation



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Paper

and/or decarboxylation of LA, leading to the formation of acetaldehyde and thus poor selectivity toward AA.^{15,21} However, the role of Lewis acids and bases during this dehydration process is still under debate. The high performance of NaY zeolites modified with rare earth metals (La, Ce, Sm and Eu) was explained by the higher content of weak acid sites.⁸ Whereas the enhanced selectivity toward AA obtained on barium doped NaY zeolites (Ba/NaY) was attributed to its high content of medium basic sites.¹³ In the KI/NaY-catalyzed dehydration of LA, it was proposed that dehydration of LA occurs on acid-base pairs, in which K⁺ ions act as Lewis acid sites and the framework oxygen plays the role of basic sites.¹⁰ Similar theory was proposed by Yuan et al. for the ZSM-5 based catalysts.¹⁸ In the study on ZSM-5 modified by NaOH and Na₂HPO₄, Zhang et al. suggested that medium acid sites and medium basic sites were important for achieving high selectivity toward AA as well as long term stability.²² However, studies on ion-exchanged β zeolites showed that weak acid and weak base sites were desired for the optimized catalysts.²³ For sulfate-based catalysts, weak acid sites were found to be important to achieve high selectivity toward AA.¹⁵ In phosphate catalyzed systems, Miller et al. indicated that the formation of metal lactate as an intermediate is a critical step during the catalytic transformation of LA to AA.^{16,17} This idea was further developed by Ghantani and co-workers, who suggested that the formation of metal lactate was accompanied by a proton transfer to the phosphate, leading to in situ generation of P-OH Brønsted acid sites.7 Therefore, the metal cation, acting as a Lewis acid site, stabilized the negatively charged carboxylic group of LA, while the P-OH group was responsible for the dehydration process.

Lanthanum phosphate (LaP) has been reported as a dehydration catalyst.^{24,25} Rod-shaped nanocrystalline LaP containing a high density of Lewis acid sites was used as a catalyst for the acetalformation reaction.²⁶ However, the catalytic capability of LaP for the dehydration of LA has not been explored yet. In this work, we report on the catalytic performance of LaP catalysts in the selective dehydration of LA to AA. LaP materials with relatively high specific surface areas were synthesized using *n*-butylamine as a shapedirecting agent (SDA). The influence of the organic SDA on the structural and surface properties of LaP materials is discussed. Also, a correlation between the acid–base properties of the LaP catalysts and their catalytic behaviour is reported.

2. Experimental

2.1 Synthesis of lanthanum phosphate materials

All chemicals were obtained from Sigma-Aldrich and used without further purification. Lanthanum phosphate (LaP) materials were prepared based on the method reported by Onoda *et al.*²⁷ In a typical synthesis process, solutions of ammonium dihydrogen phosphate (NH₄H₂PO₄) and lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) were prepared separately. A 50 wt% of ethanol aqueous solution was used as a solvent due to the low solubility of the SDA in water. The SDA was added into the solution of NH₄H₂PO₄. The dissolved La(NO₃)₃ was then introduced dropwise into the mixture of NH₄H₂PO₄ and the SDA with vigorous stirring at room temperature. A white solid precipitated immediately, and the slurry was kept stirring for 24 h. The precipitate was recovered by centrifugation, washed with deionized water copiously and then dried at 60 °C overnight. Finally, the solid was calcined at 550 °C for 4 h. The mole ratio of SDA/La was varied from 3 to 6. Accordingly, LaP catalysts were denoted as LaP-x (x = 3, 4, 5, 6), where x indicates the SDA/La molar ratio. For the sake of comparison, a LaP sample without the addition of the SDA was also prepared, and was labelled as LaP-0. To study the porosity effect of LaP materials on the catalytic dehydration of LA, a modified LaP-3 sample with a relatively low surface area was also prepared. LaP-3 was modified by loading a small amount of amorphous LaP to minimize the specific surface area by blocking its pores. The introduction of amorphous LaP was carried out by impregnating LaP-3 with $La(NO_3)_3$ and $NH_4H_2PO_4$, followed by washing, drying and calcination. The loading of amorphous LaP was 2 wt%. The modified LaP-3 was denoted as LaP/LaP-3.

2.2 Catalytic dehydration of LA to AA

The dehydration of LA was carried out using a vertical, down-flow, packed bed reactor. 0.2 to 0.5 g of LaP-x were loaded in the middle of the reactor. Before each reaction, the loaded catalyst was dried at 350 °C for 1 h under a flowing mixture of He/N₂ 5%. Nitrogen was used as the internal standard for the gas phase analysis using online gas chromatography (GC). The flow rate of the carrier gas $(He/N_2 5\%)$ was kept at 35 ml min⁻¹. 20 wt% of an aqueous solution of LA was fed and vaporized at the top of the reactor along with the carrier gas. Gas phase products, such as CO, CO2 and a fraction of acetaldehyde, were determined by an online GC (Shimadzu 2014), whereas the other products were condensed in a stainless steel trap located at the outlet of the reactor. The liquid products were analyzed by an offline GC (Agilent 6890). Fouling of spent catalysts was estimated from the weight loss after calcination. The carbon content in spent catalysts was estimated based on the method suggested by Miller et al.28 The conversion of LA and the selectivity toward AA were calculated based on the following equations:

Conversion of
$$LA = \frac{\text{fed } LA \text{ in mole} - \text{unreacted } LA \text{ in mole}}{\text{fed } LA \text{ in mole}} \times 100\%;$$

Yield of product =
$$\frac{\text{Amount of carbon in the product (mole)}}{\text{Amount of carbon in fed LA (mole)}} \times 100\%;$$

Selectivity of product =
$$\frac{\text{Amount of carbon in the product (mole)}}{\text{Amount of carbon in converted LA (mole)}}$$

× 100%

2.3 Characterization

 N_2 physisorption isotherms were measured at -196 °C on a static volumetric instrument (Autosorb-6b, Quanta Chrome). The specific surface area was estimated using the Brunauer-Emmett-Teller

PCCP

(BET) method,²⁹ and the pore size was calculated by the Barrett-Joyner-Halenda (BJH) method, using the desorption branch of the isotherms.³⁰ Powder X-ray diffraction (XRD) measurements were collected under Cu Ka radiation using a Bruker D8 X-ray diffractometer over a 2θ range of $20-80^\circ$, employing a step size of 0.017° and a step time of 1 s. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded using Bio-Rad FT-IR 3000 MX equipped with a mercury cadmium telluride (MCT) detector. Every spectrum was obtained based on 128 scans with a resolution of 4 cm⁻¹. Before each measurement, the sample was pre-treated at 200 °C in helium for 1 h to remove surface moisture and contaminants. Acid sites were evaluated using temperature programmed desorption of NH₃. In a typical NH₃-TPD experiment, 0.2 g of sample was pre-treated in helium flow at 400 °C for 2 h. Then, the temperature was lowered to 100 °C, and the sample was treated with a flowing gas mixture of He/NH₃ 5%. Afterwards, the sample was purged with helium to remove physisorbed NH₃. TPD measurements were then carried out from 100 to 450 °C using a heating rate of 5 °C min⁻¹. Transmission electron microscopy (TEM) images were captured using a Tecnai F20 equipped with a field emission electron gun and operated at 200 kV and a TEM instrument operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a XPS spectrometer (Thermo VG Scientific ESCALAB 250), using Al Ka (1486.6 eV). IR spectra of adsorbed pyridine on the catalysts were measured on a BIO-RAD spectrometer. Solid samples were pressed into a wafer and loaded in an IR cell. The wafer was treated at 300 °C under vacuum for 30 min. The background spectrum was recorded under vacuum at room temperature (RT), before collecting the spectra of samples. The wafer was then exposed to a vapor of dried and purified pyridine at RT for 30 min, followed by evacuation for 30 min at 22, 100, 200 and 300 °C, respectively. All spectra were recorded under vacuum at RT.

3. Results and discussion

3.1 Characterization of lanthanum phosphate (LaP)

The crystallinity of LaP-*x* prepared with different amounts of SDA was examined by powder XRD. As shown in Fig. 1, all LaP materials show the typical XRD pattern of rhabdophane type LaP.³¹ With increasing amounts of SDA, a new crystalline phase becomes more and more noticeable, which can be attributed to the formation of a new type of LaP mixed with a minor quantity of lanthanum oxide (La_2O_3) .^{31,32} The existence of La_2O_3 at high SDA concentration implies that the SDA may hinder the interaction of La^{3^+} and P–O⁻ during precipitation, resulting in the segregation of crystalline phases and the formation of La_2O_3 .

Generally, high surface area catalysts are preferred in heterogeneous catalysis, due to their increased density and enhanced accessibility of active sites. The porosity of LaP-x samples was examined by using N₂ physisorption. As shown in Fig. 2a, both the isotherm shape and hysteresis loop of the LaP catalysts change with the increasing amount of SDA, suggesting modification of the pore shapes. As shown in Table 1, the specific surface View Article Online



Fig. 1 The XRD patterns of LaP-*x* samples prepared using different SDA/La ratios.



Fig. 2 (a) N_2 physisorption isotherms and (b) pore size distributions of LaP-x samples.

area of LaP-3 is around 179.1 m² g⁻¹, this value being higher than that reported for lanthanum phosphate materials prepared using cetyl trimethylammonium bromide (CTAB) as an SDA (123.0 m² g⁻¹) using the same SDA/La molar ratio of LaP-3.²⁴ However, a further increase in the amount of SDA results in a decrease of the specific surface area of the LaP materials. When a SDA/La ratio = 3 was used during the synthesis, the pore size distribution is very uniform and the average pore size is around 4.8 nm (see Fig. 2b). However, increasing the amount of SDA leads to a less uniform pore-size distribution, along with an increase in

Table I Texture properties of Lap-x Catalyst	Table 1	Texture	properties of	LaP-x	catalysts
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Catalysts	s Surface area (m ² g	⁻¹) Pore volur	me (cm ³ g ^{-1}) Pore size (nm)
LaP-3	179.1	0.21	4.0
LaP-4	175.5	0.28	6.1
LaP-5	160.3	0.43	9.6
LaP-6	153.5	0.58	12.8

the average pore size (see Fig. 2b, LaP-4, LaP-5 and LaP-6). These results may also serve as evidence of the specific interaction between the SDA and LaP, which promotes the formation of LaP samples with a high specific surface area.

TEM was employed to further study the structure of the LaP-*x* samples. Fig. 3 shows that all LaP materials are in the form of aggregated nano-rods. Generally, these nano-rods are 20 to 30 nm long and 5 to 10 nm wide. No well-defined mesopores are observed. Therefore, the mesopores detected by N_2 physisorption measurement can be attributed to the formation of pores among the intercalated nano-rods. Based on the characterization results reported above, the changes in pore size distributions of the LaP materials could be explained by



Fig. 3 TEM images of LaP-*x* samples prepared using different SDA/La ratios.

the interaction between the SDA and LaP particles during the growth of LaP nano-rods. The aggregation degree decreases with the amount of SDA used, possibly because of a higher number of SDA molecules surrounding the surface of the LaP nano-rods at higher concentrations of the SDA, hence hindering the agglomeration of LaP nano-rods during precipitation. The SDA may react with residual P-OH groups on the surface, giving rise to the formation of ion pairs. The SDA may also be coordinated with the surface lanthanum cations located at defect sites of the crystals. Similar interactions between templates and calcium hydroxyapatite (CaHAP) nanoparticles have also been reported by Tanaka et al.33 Mesopores, generated by the aggregation of CaHAP nanoparticles, were also found after the removal of the template. In line with this assumption, the surface properties of these LaP materials could also be modulated by the amount of SDA, resulting in changes of crystallinity and porosity. Usually, the surface properties of the catalytic materials determine their catalytic performance.

The surface composition of LaP-x was characterized by XPS. The XPS spectra of La, P and O are shown in Fig. 4a-c, respectively. By comparing the peaks assigned to La $3d_{5/2}$, a negative shift is observed for the catalysts prepared using the SDA, which may be due to the formation of La2O3.34 Besides the change in binding energy, a change in the intensity ratio of the satellite peak to the main peak (I_s/I_m) is also observed. As shown in Table 2, this $I_{\rm s}/I_{\rm m}$ ratio gradually increases with the amount of SDA. The satellite peak at higher binding energy is attributed to the O 2p–La 4f charge transfer ending in a 3d⁹4f¹ final state.³⁵ The increase of the I_s/I_m ratio also indicates the formation of La₂O₃.³⁵ P and O peaks do not show any observable shift. Based on our XPS data and tabulated sensitivity factors, semiquantitative analyses were performed to study the chemical composition on the surface of LaP-x samples. To minimize systematic errors, atomic ratios of La/P and O/P instead of absolute compositions are listed in Table 2.



Fig. 4 XPS spectra of LaP-x: (a) La 3d_{5/2}, (b) P 2p, (c) O 1s.

Table 2 ~ $I_{\rm s}/I_{\rm m}$ ratio of La $3d_{5/2}$ and surface atomic ratio derived from XPS measurements

		Atomic ratio		
Catalysts	$I_{\rm s}/I_{\rm m}$	La/P	O/P	
LaP-3	0.79	0.52	2.25	
LaP-4	0.81	0.56	2.46	
LaP-5	0.83	0.66	2.73	
LaP-6	0.86	0.71	2.87	

Both the La/P and O/P ratios increase with the amount of SDA used during the synthesis, which confirms the formation of La_2O_3 on the surface of LaP nano-rods. These results are in good agreement with XRD results, suggesting the interaction of the SDA and LaP particles. This specific interaction promotes the formation of La_2O_3 and possibly impairs the crystallinity of LaP nano-rods, resulting in surface defects.

The acid-base properties of the catalysts play a critical role in the catalytic dehydration of LA to AA. NH₃-TPD was employed to evaluate the acidity of LaP-x materials. As shown in Fig. 5a, broad NH₃ desorption bands can be observed for all LaP-x samples between 100 and 400 $^\circ$ C, which evidences the presence of acidic sites on all phosphate samples.²⁶ The TPD signal was calibrated and the density of acidic sites was calculated based on the area of the peaks. The acid density decreases monotonically with the increasing amount of SDA, with a significant drop in acidity when the SDA/La ratio is larger than 4. These broad bands are further deconvoluted into three peaks in order to study the contribution of acid sites with different strengths. The concentration of acid sites with different strengths, derived from the deconvolution of the TPD curves, is reported in Table 3. By plotting the relative density of acid sites versus the SDA/La ratio (Fig. 5b), it is clear that all types of acid sites diminish with the increase in the SDA, but the strong acid sites decline much faster, followed by the acid sites with medium strength, while the decrease of weak acid sites is the slowest. However, the type of acid sites (Brønsted or Lewis acid sites) cannot be determined from the NH₃-TPD results.³⁶⁻³⁸



Catalysts	Total acid $(\mu mol g^{-1})$	Weak acid (µmol g ⁻¹)	Medium acid $(\mu mol g^{-1})$	Strong acid $(\mu mol g^{-1})$
LaP-3	670	328	235	107
LaP-4	603	277	211	115
LaP-5	444	244	147	53
LaP-6	375	236	113	26

To further understand the acid-base properties of the LaP-x samples, DRIFTS was also used to characterize the surface species. Before measurements, all samples were heated up to 200 °C and purged with pure N₂ for 2 h, in order to remove physically adsorbed water. In the region of OH group vibrations, ranging from 2900 to 3800 cm^{-1} (see Fig. 6a), the main peak is observed at 3510 cm⁻¹ along with two shoulders that can be detected on each side for all samples. To examine the differences among these signals, each broad absorption band was deconvoluted into three peaks. The small peak centered at 3680 cm⁻¹ can be assigned to OH groups bonded to phosphorous atoms (i.e., P-OH groups, see red dashed lines), while the main peak centered at 3500 cm⁻¹ is due to OH⁻ ions in the lattice (blue dashed lines).³³ The broad band centered at 3280 cm⁻¹ (yellow dashed lines) can be assigned to strongly adsorbed water which can only be efficiently removed above 400 °C.39

The absorption at 3680 cm⁻¹ is negligible for all LaP-*x* samples, suggesting a very low amount of P–OH groups on surfaces. The intensity of this absorption signal decreases with the increase of the SDA. This signal of P–OH groups almost disappears in the spectrum of LaP-6. The absence of P–OH groups on LaP-5 and LaP-6 could be attributed to the interaction between the SDA and LaP surfaces, which promotes the formation of La₂O₃, and thus P–OH groups may be covered by La₂O₃. This assumption is supported by the XPS results, which indicate the formation of La₂O₃ on the surfaces when the concentration of SDA increases. In addition, the formation of La₂O₃ is also evidenced by DRIFTS measurements. Absorption bands between 1400 and 1600 cm⁻¹, assignable to ν 3 carbonate modes, are found on LaP catalysts



Fig. 5 (a) NH_3 -TPD of LaP-x samples and density of acid sites; (b) relative density of acid sites with different strength *versus* the SDA/La ratio used during synthesis.



Fig. 6 DRIFTS spectra of LaP-*x* prepared with different SDA/La ratios.

prepared using a SDA.⁴⁰ The intensity of this peak increases with the addition of the SDA. These carbonate species may result from the adsorption of CO_2 from the atmosphere at strong basic sites of LaP-*x*, namely the La₂O₃ deposited on the surfaces.⁴¹

It is important to note that while acid sites are detected by NH₃-TPD, DRIFTS measurements suggest a very low content of Brønsted acidic sites (P-OH) on catalyst surface. Therefore, it can be postulated that the acid sites on LaP prepared using SDA (sample LP-3 to LP-6) are mainly Lewis acid sites. To confirm this, FTIR measurements of adsorbed pyridine were carried out to examine the nature of the acid sites of these samples. The clear peak centred around 1443 cm⁻¹ can be assigned to the adsorbed pyridine on Lewis acids.⁴² While the signal at 1484 cm⁻¹ could be attributed to both Lewis and Brønsted acids,⁴³ the signal corresponding to the existence of only Brønsted acidic sites ($\sim 1540 \text{ cm}^{-1}$) is absent for all samples. LaP-3 and LaP-4 show strong signals of Lewis acids, while the peak of Lewis acid sites becomes very weak for LaP-5. No adsorbed pyridine can be detected on LaP-6 after evacuation at 100 °C. The pyridine adsorption results may also be explained by the interaction of the SDA and phosphate during the synthesis of these catalysts. It can be postulated that these acid sites are envisaged as La³⁺ cations of LaPO₄ or La₂O₃.³⁶ When a SDA/La ratio of 3 was used, the effect of the SDA on the crystallization of LaPO₄ is small; thus almost all La³⁺ ions are balanced with PO_4^{3-} , and very few P-OH groups are formed. Thus, the Lewis acidity of LaP-3 is mainly attributed to the La³⁺ ions in LaPO₄ crystals. However, the broad band of NH₃-TPD suggests the existence of a spectrum of acid sites with different strengths on the surface of the LaP samples (see Fig. 5a). This may be attributed to the heterogeneity of the LaP crystallinity. For example, the charge of a La³⁺ ion on a well-defined LaP crystal is balanced by $\overline{PO_4}^{3-}$. Therefore, the Lewis acidity of these charge-balanced La³⁺ ions is weak. While La³⁺ ions residing at the defects of LaP crystals may exhibit strong Lewis acidity.^{36,44}

When the SDA/La ratio is higher than 4, the crystallinity on the surface of LaP nano-rods may be disturbed by the additional amount of SDA via electrostatic interactions. This may lead to the segregation of a small amount of La³⁺ cations, which eventually leads to the deposition of La2O3 on the surface of LaP nano-rods after calcination. The formation of La₂O₃ is supported by the XPS and DRIFTS results. These La₂O₃ species could cover the Lewis acid sites on the surface of the samples when high SDA/La ratios are used, leading to a decrease in the density of acid sites (see Fig. 5a). The presence of SDA may also promote the formation of defects on the surface of LaP-4, and thus more strong acid sites on LaP-4 are formed, which may explain the slight increase in strong acid sites (see Fig. 5b) when the SDA/La ratios are increased from 3 to 4. The increase in defects may also improve the accessibility of La³⁺ cations. As a result, the signal of pyridine adsorbed onto Lewis acids in LaP-4 is higher than that of LaP-3 (see Fig. 7). A further increase of the amount of SDA results in the deposition of excess La₂O₃ which covers the acid sites and hinders the adsorption of pyridine. NH₃-TPD of LaP-5 and LaP-6 shows a desorption peak which indicates that NH3 are adsorbed on LaP-5 and LaP-6.



Fig. 7 $\,$ FTIR spectra of adsorbed pyridine after evacuation at 100 $^\circ C$ on LaP-x samples.

This could possibly be due to the smaller molecular size of NH_3 compared to that of pyridine. As shown in Fig. 5b, the decreasing rate of the amount of acid sites with different strengths is in the following order: strong > medium > weak. Possibly because the strong Lewis acidic sites, *i.e.*, La^{3+} ions located at defects, are more unstable and easily converted to La_2O_3 .

In order to get more insight into the effect of Brønsted acids, a catalyst with a higher concentration of Brønsted acids was also prepared without the addition of the SDA. This sample was denoted as LaP-0. This was inspired by the DRFTS results, where the signal of P–OH groups is inversely proportional to the amount of SDA used. As shown in Fig. S1 in the ESI,† the DRIFTS signal of P–OH groups on LaP-0 is significantly larger than that of LaP-3, suggesting the presence of a higher density of Brønsted acids. The distinct acidity of LaP-0 may arise from the low pH value (\sim 1) during the synthesis of this sample.

3.2 Dehydration of lactic acid (LA) to acrylic acid (AA)

The catalytic performance of LaP-*x* samples was tested in the dehydration of LA to AA. Table 4 summarizes the catalytic results. Among these catalysts, LaP-3 shows the highest selectivity toward AA, while the highest conversion is obtained on LaP-4. Further increasing the amount of SDA during synthesis leads to poorer catalytic results and serious fouling.

For the sake of comparison, a sample with higher Brønsted acidity was also tested (LP-0, see the ESI,† Table S1). A very high conversion is obtained on LaP-0, while the selectivity to AA is about 10% lower than that of LaP-3. As Ghantani *et al.* suggested,⁷ Brønsted acids (P–OH groups on phosphates) could facilitate decarbonylation, resulting in the formation of acet-aldehyde, which undermines the selectivity towards AA.

The catalytic performance is usually determined by both physical and chemical properties. In the LaP system, the different behaviours on the dehydration of LA could be attributed to the structural and surface properties. From N₂ physisorption analysis (Table 1), LaP-3 exhibits the highest surface area, along with the highest selectivity toward AA (Table 4). To understand the effect

 Table 4
 Catalytic results of the dehydration of lactic acid to acrylic acid using LaP-x catalysts

		Selectivity (%)						
Catalysts ^a	Conversion (%)	Acrylic acid	Acetaldehyde	2,3-Pentanedione	Propanoic acid	Others ^b	Fouling ^c	Carbon balance
LaP-3	67.4	49.6	21.2	0.2	3.1	20.8	2.8	97.7
LaP-4	72.0	46.9	25.3	0.2	2.2	14.7	4.7	94.0
LaP-5	60.4	27.5	24.2	0.4	6.9	22.8	9.2	91.0
LaP-6	53.1	7.9	26.0	0.4	7.4	27.7	12.9	82.3
LaP/LaP-3	63.8	42.7	25.7	0.1	1.4	18.0	1.7	89.6

^{*a*} All results are based on 5 measurements of time on stream (TOS), reaction temperature: 350 °C, LA concentration: 20 wt%, catalyst loading: 0.2 g. ^{*b*} Others include acetic acid, ethanol, hydroxyacetone and CO. ^{*c*} Fouling is estimated from the weight loss after calcination of spent catalysts.

of surface area a LaP-3 sample with a relatively low surface area was prepared. The porosity of LaP-3 was undermined by loading a small amount of amorphous LaP (2 wt%) on the catalyst using an impregnation method. This sample was labelled as LaP/LaP-3. Based on N₂ sorption measurements, a sharp decrease in both the surface area (from 179.1 to 109.4 m² g⁻¹) and the pore volume (from 0.21 to 0.08 m³ g⁻¹) is observed upon impregnation of LaP-3 with additional LaP. However, the significant change in porosity only has a very limited influence on the catalytic performance, as shown in Table 4. This indicates that the porosity of the catalyst is not a determining factor for LaP-based catalysts.

Hence, the effect of acid and basic sites on the dehydration of LA over LaP was evaluated. Based on the characterization of the acid-base properties and the catalytic results, it is clear that Lewis acid sites are crucial to obtain a high yield of AA. The positive effect of Lewis acids has also been reported in the KI/NaY-catalyzed dehydration of LA. The enhancement of selectivity was related to the weakened Lewis acidity due to the presence of $K^{+,10}$ A similar conclusion was also drawn for LA dehydration over Ba/NaY.¹³ In the present case, the La³⁺ cations of LaPO₄ act as Lewis acids. Correlations can be found between the catalytic performance and the amount of Lewis acid sites with different strengths. A good linear correlation between the catalytic performance and the amount of strong acid sites is shown in Fig. 8, indicating that these acid sites play a key role in the selective dehydration of LA to AA.

Basic sites lead to by-products and fouling. The carbonaceous species deposited on the catalysts can block the active sites, therefore inhibiting the dehydration process. The colour of the catalysts changed from white to light brown, suggesting that the deactivating carbon deposit consists not only of carbon-containing species but also other components, possibly oxygenated species.²⁸ Thus the carbon balance becomes poor for LaP-6 which contains a higher density of strong base sites.

As summarized in Scheme 1a, Lewis acid sites, mainly La^{3+} cations of $LaPO_4$, play a critical role in the dehydration of LA over LaP-*x*, while strong base sites cause carbon deposition on the catalysts. The catalytic mechanism may be similar to that proposed for the dehydration of LA over CaHAP.⁷ As shown in Scheme 1b, the carboxylic group of LA interacts with La^{3+} and transfers a proton to the phosphate, leading to the *in situ* formation of a P–OH group. Therefore, La^{3+} stabilizes the carboxylic group of LA avoiding the production of acetaldehyde,



Fig. 8 Correlation between the density of strong Lewis acid sites and the catalytic performance.

while the P–OH group catalyzes the dehydration of the adsorbed LA to AA. Finally, the AA is desorbed by accepting a proton from an adjacent P–OH group or another LA.

From the viewpoint of application, stability is an important attribute in industrial applications. A long-term catalytic dehydration test of LA was carried out using the most promising catalyst, LaP-3. These results are plotted in Fig. 9. A stabilization period of roughly 5 h is required to achieve steady-state conditions. This induction period may cause the adsorption/saturation of the catalyst using LA and AA. Similar observations have also been reported by others.¹⁷ As shown in Fig. 9, the conversion decreases with the TOS due to fouling. However, the decrease in conversion becomes slower and the conversion level seems to be stable at around 70%, leading to a pseudo-steady state at the end of the catalytic test. It is interesting to note that the selectivity increases gradually from 45% to 52% and seems to reach a pseudo-steady state level after 28 h. This is probably due to the preferential deposition of carbon species on the active sites that are responsible for the side reactions such as the basic sites which promote the formation of polylactate.⁶ Overall, the yield of AA remains around 40%, after the induction period. The long-term stability of LaP-3 can be ascribed to the low density of basic sites, preventing the fast formation of carbonaceous deposits on the catalyst.





Fig. 9 Stability test of LaP-3 during the dehydration of LA. Reaction temperature: 350 $^\circ$ C, catalyst loading: 0.5 g, LA concentration: 20 wt%.

4. Conclusions

In the present study, LaP-*x* samples with a high specific surface area were prepared using *n*-butylamine as a SDA. Both mesoporous structural and surface properties are affected by varying the amount of SDA. The porosity of the LaP catalysts shows a very limited influence on the dehydration of LA to AA. Instead, the acid–base properties of the LaP catalysts significantly affect the catalytic performance. A combination of characterization techniques reveals that Lewis acids on LaP materials, mainly La^{3+} cations, play an essential role in the catalytic dehydration of LA to acrylic acid, while basic sites are responsible for catalyst deactivation.

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