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ARTICLE

Highly active tin (IV) phosphate phase transfer catalysts for the production of lactic acid from triose sugars†

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Lactic acid (LA) is an important intermediate in the fine chemical industry because it is utilized as a building block for the production of biodegradable plastics. In this study, a series of tin phosphate phase transfer catalysts modified with several surfactants have been prepared by a facile one-pot synthesis method and tested for the direct conversion of trioses to LA under hydrothermal conditions. Poly(ethylene glycol) (PEG) was identified as the most promising surfactant, and the product distribution closely depended on the reaction temperature, catalyst loading and substrate concentration. Complete DHA conversion and a good yield of up to 96.1% of LA were obtained at 140 °C after 4 h of reaction time. Pyridine FTIR demonstrated the presence of Brønsted and Lewis acid sites, which play crucial roles in the dehydration of DHA to pyruvaldehyde (PA) and the following isomerization of generated PA to LA. Furthermore, the isomerization of PA to LA was found to be the rate-determining step. A possible reaction mechanism was proposed: 1) the coordination between PEG and the metal ions caused a greater separation of the tin ions from the phosphate anions, making them more potent Lewis acid sites, and 2) the PEG behaved as a phase transfer catalyst during the reaction. This study paves the way for the further design of improved solid acid catalysts for aqueous phase production of LA from carbohydrates.

Introduction

The unsustainable dependence on fossil fuels for energy and chemicals has stimulated a worldwide initiative to develop clean technologies that utilize a sustainably produced feedstock.[1] Carbohydrates are abundant and inexpensive feed stocks that have received considerable attention as sustainable alternatives for the production of fuels and platform chemicals.[2] One of the key building blocks that can be obtained from carbohydrates is lactic acid (LA), which has been identified as a versatile commodity chemical with various applications, including in the food, cosmetics and pharmaceutical industries.[3] LA is also a building block in the production of biodegradable polymers (polylactic acid) with a low environmental impact.[4]

Industrially, LA is produced via the fermentation of carbohydrates by using genetically modified enzymes.[5] However, biotechnological processes suffer from many defects, such as limited space-time yields, the need for control over the fermentation conditions in the reactor (temperature or pH), high waste production, and population control

regulations for the microorganisms. Therefore, developing novel chemo-catalytic methods for the direct conversion of carbohydrates to LA have recently attracted additional attention in both academia and industry.[6]

Dihydroxyacetone (DHA), which can be obtained by the stoichiometric or catalytic oxidation of glycerol or by the fermentation of glycerol, is a low-cost precursor for the production of LA and is commonly used to study the effects of various catalysts because it has a fundamental carbon structure similar to that of LA.[7, 8] Moreover, previous studies have implied that DHA is an important intermediate when converting C6 sugars into LA.[9] These findings have stimulated research activities on the conversion of DHA into LA. Several homogeneous catalysts, such as H_2SO_4,[10] $Ca(OH)_2$,[11] $CrCl_3 \cdot 6H_2O$,[12] $ZnSO_4$,[13] $AlCl_3 \cdot 6H_2O$,[12, 14] $SnCl_2$,[12, 15] and $SnCl_4 \cdot 6H_2O$,[12] have been found to be efficient for the transformation of DHA into LA and its esters. Rasrendra et al. screened a wide range of homogeneous catalysts, in the form of metal salts, for the conversion of DHA and glyceraldehyde (GLA) to LA in aqueous solutions; they determined that Al^{III} and Cr^{III} salts were the most promising catalysts, with LA yields up to 93 mol%.[16] However, the major obstacles for the application of homogeneous catalysts are the separation of the homogeneous catalysts from the products and the extremely harsh conditions.

Therefore, heterogeneous catalysts that possess the advantage of the facile separation of catalysts from the products by filtration have been explored for the synthesis of LA or alkyl lactates from trioses. High yields of LA were achieved at 125 °C for Sn-Beta zeolite[17] (90 mol%) and an

ultrastable-Y zeolite (H-USY)[15] (71 mol%) from the conversion of DHA in water after 24 h. A relatively high selectivity for LA (83%) at 92% DHA conversion was achieved at 110 °C after 6 h over the Sn-Si-CSM catalyst.[18] Dapsens et al.[19] reported that desilicated ZSM-5 in solutions of alkali metal hydroxides attained a LA selectivity exceeding 90% (up to 92%). However, zeolites and related materials usually suffer from hydrothermal instability in aqueous systems. Therefore, alcohols were used as solvents for the synthesis of alkyl lactates from trioses. Taarning and co-workers reported that Sn-based catalysts (Sn-Beta zeolite) were suitable catalysts for the conversion of hexoses or trioses to methyl lactate in methanol; they also reported that a 99 mol% yield was obtained when using DHA as a substrate.[17, 20] The use of commercial available ultrastable Y (USY) zeolites has also been studied for the conversion of trioses to alkyl lactates, with promising yields (up to 96 mol%).[15, 21] Onaka et al.[8] reported the use of tin ion-exchanged montmorillonite (Sn-Mont) for the conversion of DHA, with alkyl lactate yields of 89-93 mol%. Quantitative and selective production of alkyl lactates has been obtained by Sels et al. using Sn-MCM-41[22] or Sn-Si-CSM-773[18] in ethanol at 90 °C, with 98% or 100% selectivity at 100% DHA conversion. Lactic acid esters have been obtained with high yields of nearly 100% in alcohol solvents.[23] However, exploratory studies aimed at the development of an efficient heterogeneous catalyst for the conversion of trioses to LA using water as a solvent have not been intensively conducted, especially considering that utilizing environmentally benign solvents in chemical reactions is one of the most interesting areas in green chemistry.[24] The main challenge of using water as a solvent is the formation of undesired byproducts and the relatively low yields.[6]

The metal-catalyzed studies discussed above have indicated that metal cations could efficiently catalyze the reactions of trioses to LA. The reports on the tin-derived catalysts of Sn-Beta, Sn-Mont, and Sn-MWW,[25] as well as the reports on the acidic ultrastable-Y zeolites, prompted us to investigate the catalytic efficiencies of tin phosphates (SnP) for the conversion of DHA to LA in aqueous reaction media. Indeed, large-pore mesoporous aggregated tin phosphate nanoparticles, which were synthesized under hydrothermal conditions by using Pluronic P123 as the structure-directing agent, have been successfully used for the conversion of sugars to 5-hydroxymethylfurfural (5-HMF) in water/methyl isobutyl ketone biphasic solvents.[26] Moreover, Alamillo et al. reported that organic-inorganic nanocomposite synthesized by intercalation of poly(vinylpyrrolidone) (PVP) into the ordered mesopores of acid-functionalized silica could selectively convert fructose into 5-HMF in a flow reactor.[27]

In the present study, Pluronic P123, together with another Pluronic template, F127, was used during the synthesis of SnP. Moreover, poly(ethylene glycol) (PEG) and its derivatives that have chain structures similar to those of the Pluronic templates previously described have already been used for various transformations because they are nontoxic, inexpensive, nonionic, thermally stable and recoverable liquid solvents of low volatility.[28] Herein, PEG with varying molecular
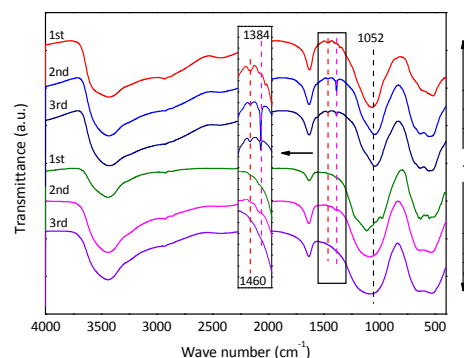

Fig. 1 FTIR spectra of the as-synthesized and calcined SnP-PEG2000 during three consecutive runs (Inset: enlarged graph corresponding to the black rectangle).

weights and poly(ethylene glycol) dimethyl ether were also introduced to the synthesis of SnP. Tin phosphates, with or without surfactants, have been successfully synthesized and used catalytically during the hydrothermal conversion of trioses to LA. SnP-PEG2000 was identified as the most promising catalyst, and the yields were optimized by the variation of process conditions, including temperature, catalyst loading and DHA concentration. In addition, a possible reaction mechanism involving the phase transfer catalytic method was postulated and supported by other non-polymer low molecular weight phase transfer catalysts, such as cyclodextrin, tetrabutyl ammonium bromide, and hexadecyl trimethyl ammonium bromide. Phase transfer catalysts already have an extensive application in organic synthesis,[29] and the introduction of them to the conversion of carbohydrates would certainly broaden their scope. In addition to the high catalytic activity and various virtues that PEGs possess, SnP-PEG has been identified as a promising material for potential industrial applications.

Results and discussion

Characterization of the SnP-PEG2000

Orthophosphoric acid and water were chosen as the phosphate source and the solvent to synthesize the tin phosphates. The FT-IR spectra of both the as-synthesized and the calcined SnP-PEG2000 show a sharp band centered at approximately 1052 cm^{-1}, which corresponds to the asymmetric Sn-O-P stretching vibration, indicating the presence of a phosphate framework (Fig. 1).[30] The bands at 1384 cm^{-1} and 1460 cm^{-1} that corresponds to C-C vibrations and the C-H bending vibration of methylene groups of surfactant molecules were absent in the calcined material, indicating the complete removal of the PEG2000 upon calcination.[26]

Table 1 Characterization of the SnP-PEG2000 by adsorption, pyridine FTIR, ICP and XPS studies.

Catalyst	BET surface area ($m^2\,g^{-1}$)	Total acid sites ($mmol\,g^{-1}$)[a]	Lewis acid sites ($mmol\,g^{-1}$)[b]	Brønsted acid sites ($mmol\,g^{-1}$)[b]	P/Sn^{IV} molar ratio[c]	Surface atomic composition[d]			
						Sn	P	O	P/Sn^{IV} molar ratio
As-synthesized	169.6	1.39	0.86	0.53	0.71	19.3	12.9	67.8	0.67
Calcined	287.3	0.82	0.72	0.096	0.67	19.7	13.3	67.0	0.68

[a] Determined from ammonia TPD.
[b] Determined from pyridine FTIR.
[c] Determined from ICP.
[d] Based on the XPS line areas of Sn 3*d*, P 2*p* and O 1*s*.

The SnP-PEG2000 was confirmed to be amorphous by PXRD (Fig. S1 and Fig. S2), and further evidence was found from the magnified views of the TEM images (Fig. S3). The morphology of SnP-PEG2000 tended to become less compact and possessed the appearance of nanoparticle aggregation after calcination. The characterization of SnP-PEG2000 by BET, ICP and XPS appears in Table 1. The calcined material possessed a BET surface area of 287.3 $m^2\,g^{-1}$, which is higher than that of the P123 modified tin phosphates previously reported (216 $m^2\,g^{-1}$);[26] however, the as-synthesized one possessed an appreciably lower BET surface area of 169.6 $m^2\,g^{-1}$. The phosphorus to tin(IV) molar ratios obtained from ICP analysis, which are comparable to those reported by Weingarten et al.,[31] are different from those used in the precipitation solutions; moreover, the molar ratios of the two SnP-PEG2000 samples were comparable to each other, and a similar trend was observed from the XPS analysis of the surface composition.

Fig. 2a shows the high resolution XPS spectra of tin for SnP-PEG2000. The Sn 3d line is composed of two peaks assigned to Sn $3d_{5/2}$ and Sn $3d_{3/2}$ at approximately 487 eV and 496 eV, respectively, which is characteristic of tetravalent tin.[32] A slight downward shift in the Sn 3d binding energies was observed for the calcined SnP-PEG2000, indicating a reduced polarization of Sn-O bonds, which could be due to fewer electronegative oxygens on the surface relative to the as-synthesized samples.[33]

The UV-vis DRS spectra of SnP-PEG2000 and SnO_2 are presented in Fig. 2b. Both the as-synthesized and calcined SnP-PEG2000 shows a maximum intensity at 220 nm arising from isolated tetrahedral Sn^{IV} species, which is often assumed to be the catalytically active sites, while the calcined SnO_2 shows a broad electronic absorption between 200 and 300 nm due to octahedrally coordinated tin species.[34, 35]

The SnP-PEG2000 was also characterized by solid-state ^{31}P MAS NMR spectroscopy (Fig. 3). An obvious transition of the chemical shift (δ_p) to more negative values after calcination was observed, indicating an increase in the chain length of the phosphorus atoms that corresponded with a progressive deprotonation and subsequent condensation of the phosphate species (P-O-P bonds) that typically occurs during calcination.[36] The as-synthesized SnP-PEG2000 possessed relatively broad peaks, which is related to the amorphous nature of the

material.[37] The resonance peak at -12.9 ppm was assigned to phosphorus with an undissociated P-O-H group.[38]
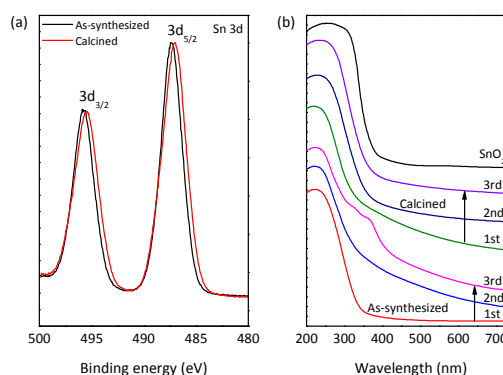

Fig. 2 (a) Sn 3d core level spectra of the as-synthesized and calcined SnP-PEG2000. The BE scale was calibrated with respect to the C 1s peak. (b) UV-vis DRS spectra of SnO_2 and the as-synthesized and calcined SnP-PEG2000 during three consecutive runs.
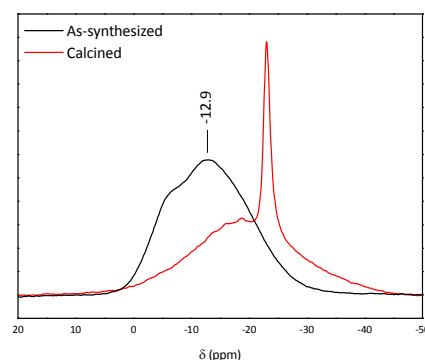

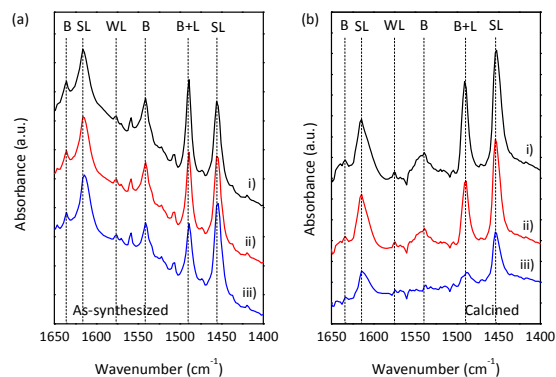**Fig. 3** ^{31}P NMR spectra of SnP-PEG2000.

Fig. 4 FTIR spectra of SnP-PEG2000 in fingerprint domain after pyridine sorption and evacuation at (i) 100 °C, (ii) 150 °C and (iii) 200 °C. Absorbance peaks characteristic of strong Lewis (SL), weak Lewis (WL), Brønsted (B) and Lewis (L) sites are indicated.

Acidity measurement

The acidic properties of SnP-PEG2000 were monitored with FTIR after pyridine chemisorptions while combined the results with acidity measurements from NH_3-TPD. Vibrations characteristic of pyridine sorption on Lewis acid sites (denoted with L) were identified at 1455 (strong LA), 1615 (strong LA) and 1576 cm^{-1} (weak LA) in accordance with the literature.[18] The strong Lewis acid strength could be reflected by the strong bonded chemisorbed pyridine after heating of the sample at 200 °C.[39] The generation of Lewis acidity is ascribed to the formation of tin in tetrahedral coordination within the SnP framework. An extra band corresponding to the overlap of the Brønsted and Lewis acid sites was observed at 1489 cm^{-1}.[40] The material also exhibited bands at 1540 and 1635 cm^{-1}, which could be attributed to the adsorbed pyridine at the Brønsted acidic sites.[15] With an increase in temperature to 200 °C, these bands showed only a slightly decrease in intensity for the as-synthesized SnP-PEG2000, indicating that these Brønsted acid sites are of strong character (Fig. 4a). However, weak Brønsted acid sites were observed for the calcined material because of the gradual disappearance of these bands under termal treatment at increasing temperature (Fig. 4b). The relative Brønsted and Lewis acidity ratio could be obtained from integrating the areas under the bands at 1540 cm^{-1} and 1455 cm^{-1} while taking the extinction coefficients into account. Using values of $\varepsilon_{Brønsted}$ =1.88 and ε_{Lewis} =1.42 as reported by Emeis,[41] values of B/L ratio of 0.616 for the as-synthesized and 0.133 for the calcined SnP-PEG2000 were obtained. NH_3-TPD revealed a higher concentration of total acid sites for the as-synthesized SnP-PEG2000 compared to the calcined one (1.39 mmol g^{-1} versus 0.82 mmol g^{-1}). Consequently, the total number of Brønsted acid sites per gram of SnP-PEG2000 is much larger for the as-synthesized one as compared to the calcined one (0.53 mmol g^{-1} and 0.096 mmol g^{-1}, respectively).
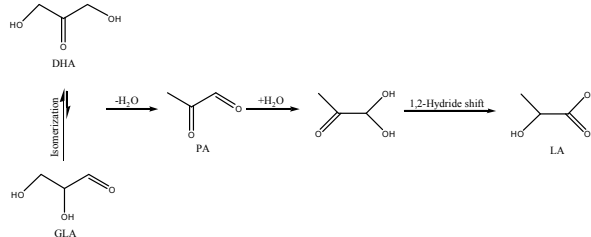
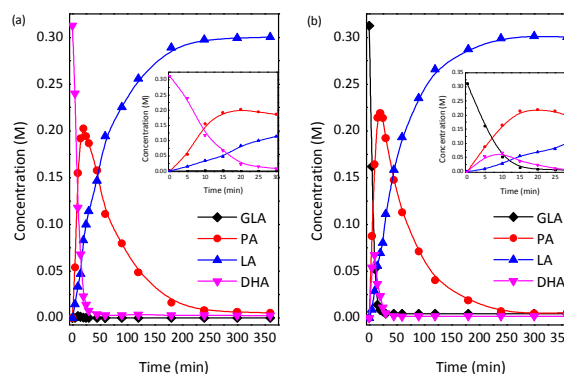**Scheme 1** Conversion of DHA and GLA to LA.

Fig. 5 Batch concentration profiles for the reactions of DHA and GLA in water. (a) 1.25 mmol DHA in 4.0 g water at 140 °C with 80 mg SnP-PEG2000. (b) 1.25 mmol GLA in 4.0 g water at 140 °C with 80 mg SnP-PEG2000 (Inset: details for GLA, DHA, PA, and LA for the first 30 min of the reaction).

Catalysis

The isomerization of the two trioses DHA and GLA into LA over an acidic SnP catalyst has been investigated. Product formation in a typical batch experiment was monitored as a function of reaction time. Concentration profiles of the initial trioses are shown in Fig. 5. Both GLA and DHA were observed when either substrate was used as a starting reagent, indicating that the isomerization between these two sugars occurred. West et al.[15] reported that DHA reacted more quickly than GLA, and Rasrendra et al.[16] identified a reverse trend. However, a similar reaction rate for DHA and GLA was observed in the present work.

Starting from DHA, only a trace amount of GLA was observed. PA had a clear optimum and reached a yield as high as 64.8% in approximately 30 min along with the complete conversion of DHA (Fig. 5a). It is worthwhile mentioning that the optimum yield of PA was only approximately 10% according to previous studies.[15, 16] The yield of LA increased with a prolonged reaction time afterward, and it reached a plateau in 4 h with a yield of 96.1%. Fig. 5b shows that the concentration of GLA declined rapidly as a transient amount of DHA appeared, thereby supporting the idea that DHA was an initial product formed by GLA.[12] An optimum DHA yield of 21.5%, which is much lower than that reported previously (approximately 60%) by West et al.[15] and Rasrendra et al.,[16]

was obtained. PA was an intermediate product, and it possessed a clear optimum that is typically observed with a consecutive reaction pathway. At longer reaction times, DHA and PA reacted further to form LA. Therefore, a reaction sequence for the conversion of GLA to LA was proposed and is given in scheme 1.

The synthetic process of the current solid acid catalysts was very simple because it avoided a time consuming crystallization procedure, especially compared with that of the commonly used zeolites and other related materials for the conversion of carbohydrates.[18] The optimum yield of LA (96.1%) was among the most promising yields in aqueous phase reported to date,[6] and it was even comparable to those obtained in alcohol solvents described in the introduction section. These findings very effectively demonstrated the ability for the production of LA from carbohydrates through the use of an environmentally benign solvent-water solution.

Effect of varying the surfactants on the production of LA

The catalytic effectiveness of tin phosphate materials with and without surfactants was investigated for the conversion of trioses into LA under hydrothermal conditions. To enable direct comparisons of selectivity, each reaction was conducted till the DHA conversion was ca. 50%. For comparison, the reaction was initially carried out in the absence of a catalyst and using phosphoric acid. A tiny amount of LA was obtained from the blank reference. When using phosphoric acid, the major product was PA, implying that H^+ ions have a positive effect on the dehydration of DHA. For each of the as-synthesized tin phosphates, the selectivities of PA (approximately 80%) and LA (approximately 20%) were significantly higher than for the corresponding calcined catalyst, with only SnP-IMEP and SnP-CTAB possessing a significant difference. Furthermore, the selectivity of LA obtained from tin chloride pentahydrate was much lower than those obtained from

the synthesized solid tin phosphates (Table 2, entry 3). Rasrendra et al.[16] also found that tin salts could give a quantitative conversion of DHA; however, the selectivity for the tin salts was always below 25%, even with a much more diluted substrate (0.1 M DHA) at 140 °C after 90 min, making it a less attractive catalyst.

P123 and F127 are two common types of polyethers that are generally used as templates for the synthesis of zeolites such as SBA-15 and SBA-16. In this contribution, the utilization of the as-synthesized materials, SnP-P123 and SnP-F127, resulted in considerable LA selectivities of 20.8% and 18.3%, respectively. The crystallization of SnP-P123 did not necessarily promote the catalytic performance, suggesting that a greatly simplified synthesis procedure was adopted here (Table 2, entry 7 vs. entry 6). Moreover, PEG and NHD represent the most simple, economic, and efficient acyclic polyethers that are used as phase transfer catalysts.[42] Considerable LA selectivities of 18.7% and 22.3% were obtained by using the as-synthesized SnP-PEG2000 and SnP-NHD at 140 °C. Several commonly used phase transfer catalysts other than polyethers, such as CD, TBAB, and CTAB, were also introduced in the synthesis of the tin phosphates, and the catalytic performance varied only slightly compared with PEG2000 except for CTAB. Therefore, the introduction of surfactants during the synthesis of tin phosphates efficiently promoted the catalytic performance of the tin phosphates for the conversion of DHA to LA.

The turnover frequencies (TOF based on total acid sites) were calculated to investigate the effect of surfactant (Table 2). For each of the surfactant-modified catalysts, the TOF was higher than for the corresponding calcined catalyst, indicating that the observed changes in reactivity with varying surfactants were due to a fundamental change in activity of the available sites. However, the TOFs obtained here are significantly lower than that of Sn-Beta.

Table 2 Catalytic conversion of DHA to LA by tin materials with various surfactants. ([DHA]$_o$=0.3125 M; Catalyst=80 mg; T= 140 °C).

Entry	Catalyst	As-synthesized				Calcined				
		t (min)	DHA Conv. (%)	PA (%)	TOF^b (h^{-1})	t (min)	DHA Conv. (%)	PA (%)	LA (%)	TOF^b (h^{-1})
1	Blank	75	51.2	53	<0.5	-	-	-	-	-	-
2	H$_3$PO$_4$	30	50.7	62.5	<0.5	-	-	-	-	-	-
3	SnCl$_4$·5H$_2$O	30	59.4	74.2	6.7	-	-	-	-	-	-
4	SnP	15	57.2	81.7	15.4	47.7	15	52.8	79	14.1	49.3
5	SnP-IMEP	15	53.1	80.5	15.8	40.5	12	50.4	81.7	13.8	53.2
6	SnP-P123	8	55.6	74	20.8	48.6	10	45.3	78.8	16.5	41.9
7	SnP-P123^a	6	54.1	71.9	21.4	42.1	10	46.7	72.3	16.2	40.4
8	SnP-F127	8	48.6	74.9	18.3	36.9	12	51.4	81.7	14.4	37.3
9	SnP-PEG2000	8	50.1	74.7	18.7	35.2	30	43.7	80.7	15.3	28
10	SnP-NHD	6	53.6	72.1	22.3	43.6	30	45.5	75.2	14.7	29.8
11	SnP-CD	6	49.6	77.2	21.6	43.9	15	53.9	81.4	15.5	38.7
12	SnP-TBAB	8	48.7	79.3	18.4	35.3	15	49.2	79.5	16.7	33.4
13	SnP-CTAB	15	48.9	79.6	15.9	32.5	10	53.1	78.2	16.4	65.2
14	SnO$_2$	-	-	-	-	-	180	49.5	4.3	6.9	-
15	Sn-Beta	-	-	-	-	-	45	46.2	13.1	67.2	175

^{a} Large-pore mesoporous SnP, ^{b} TOF=turnover frequency. (mol DHA$_{converted}$ per mol acid sites per hour at 15 min).

Table 3 Catalytic conversion of PA to LA by tin materials with various surfactants. ([PA]$_o$=0.3125 M; Catalyst=80 mg; T= 140 °C).

Entry	Catalyst	As-synthesized			Calcined		
		t (min)	PA Conv. (%)	LA (%)	t (min)	PA Conv. (%)	LA (%)
1	Blank	150	50.6	<0.5	-	-	-
2	H$_3$PO$_4$	120	49.3	4.1	-	-	-
3	SnCl$_4$·5H$_2$O	60	48.7	27.9	-	-	-
4	SnP	60	54.7	53.6	45	49.2	50.3
5	SnP-IMEP	45	50.3	58.6	45	45.7	54.5
6	SnP-P123	45	47.2	76.5	60	53.8	63.4
7	SnP-P123[a]	45	46.5	75.7	45	43.5	55.8
8	SnP-F127	30	56.4	70.4	45	49.7	59.3
9	SnP-PEG2000	45	54.7	72.4	90	51.8	60.8
10	SnP-NHD	30	50.1	78.3	60	46.2	56.2
11	SnP-CD	30	45.7	72.1	30	41.6	58.8
12	SnP-TBAB	45	52.6	71.5	45	53.3	51.6
13	SnP-CTAB	30	54.2	66.6	30	51.7	76.7
14	SnO$_2$	-	-	-	90	54.3	9.4
15	Sn-Beta	-	-	-	6	56.8	81.7

[a] Large-pore mesoporous SnP.

The performance of these materials for the conversion of PA to LA was also evaluated. The reactions were conducted by using a 0.3125 M PA solution containing 80 mg catalyst at 140 °C (results are shown in Table 3). For SnP without surfactants, the selectivity of LA was relatively low (53.6%), and brown insoluble products were formed. The calcined material of each tin phosphate catalyst tended to result in a much lower LA selectivity than the corresponding as-synthesized catalyst. Moreover, the selectivity of LA catalyzed by tin chloride pentahydrate was below 30%, and phosphoric acid was demonstrated to be the least effective catalyst. Comparing the results of PA with DHA, it seems that DHA was more efficiently converted with quantitative yields of PA. A very similar selectivity toward LA was obtained using either GLA or DHA as the substrate (Table S1).

The PEGs might be more efficient phase transfer agents by making them more soluble in the organic phase. The enhancement in solubility could be achieved by converting the PEGs to their alkyl ethers.[42] Indeed, the selectivity of LA catalyzed by SnP-NHD was higher than those obtained from SnP-PEG2000 (Table 2, entry 10 vs. entry 9). The same tendency was observed when PA was used as the substrate (Table 3, entry 10 vs. entry 9). Furthermore, the better catalytic activity of SnP-P123 over SnP-F127 could also be due to the better solubility of P123 in organic phase, because of the greater ratio of lipophilic groups of P123 than that of F127 (Table 2, entries 6 and 7 vs. entry 8).

Sn-Beta, one of the state-of-the-art heterogeneous catalysts for the conversion of carbohydrates,[20] was chosen to benchmark the performance of the SnP. The Sn-Beta resulted in a selectivity of LA superior to those of SnP with surfactants, whereas the selectivity of PA was significantly lower (Table 2, entry 15 vs. entries 6-12). The conversion of PA to LA was

effectively catalyzed by Sn-Beta with a selectivity of 81.7% (Table 3, entry 15). This is consistent with previous reports that the dehydration of DHA is the rate-determining step when catalyzed by Sn-Beta. The initial reaction rates of DHA obtained here are much higher than those reported by West et al. under similar conditions; however, the reaction rates of PA are significantly lower.[15] The initial measured rates obtained for the appearance of intermediate PA were actually the apparent reaction rates (Table S2), which were even higher than the disappearance rates of PA given in Table S3, indicating that the isomerization of PA was the rate-determining step as discussed below.

Effect of process conditions for the as-synthesized SnP-PEG2000 catalyzed reaction of DHA to LA

In the present study, the yields of LA catalyzed by the tin phosphates with various surfactants were comparable to those catalyzed by Sn-Beta. Only in the cases of SnP-IMEP and SnP-CTAB were poor results obtained (Fig. S4 shows the results after a prolonged reaction time of 6 h). Due to the fact that PEG2000 is less expensive and less toxic than the other investigated surfactants, SnP-PEG2000 was selected for further focused studies on the conversion of DHA to LA.

The conversion of DHA was strongly dependent on the reaction temperature (Fig. 6a). Essential quantitative conversions of DHA (99%) were achieved within 20 min at the highest temperature in the range (160 °C). At lower temperatures, the rate was reduced considerably, and for instance, a reaction time of 2 h was required for 98% DHA conversion at 120 °C. Fig. 6b shows the LA yields as a function of reaction time at different temperatures with SnP-PEG2000 as the catalyst. Obviously, the reaction temperature
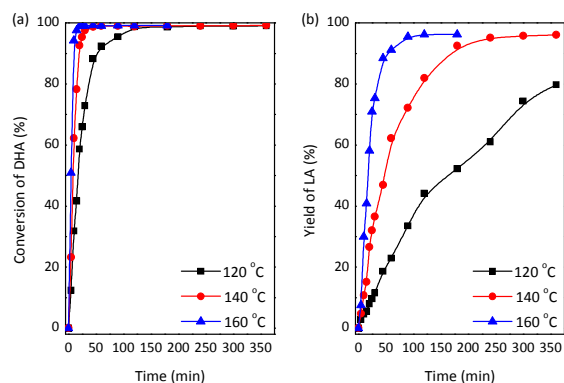
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Fig. 6 Effect of varying the temperature and reaction time on the conversion of DHA to LA with SnP-PEG2000 (conditions: 0.3125 M DHA, 80 mg SnP-PEG2000).
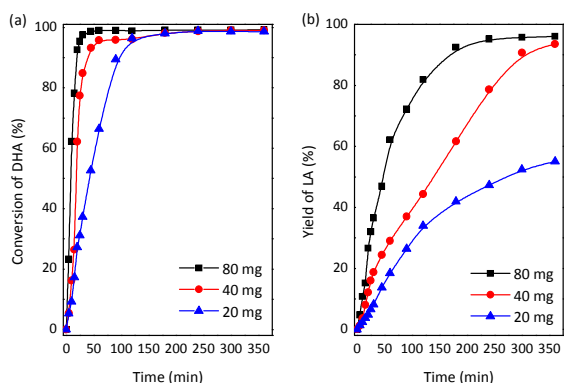

Fig. 7 Effect of the SnP-PEG2000 dosage on the conversion of DHA to LA (conditions: 0.3125 M DHA, 140 °C).
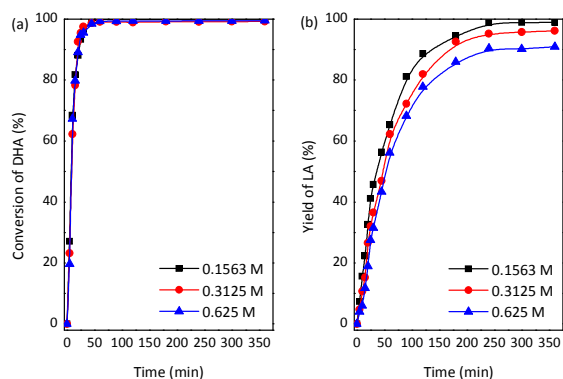

Fig. 8 Effect of the initial concentration on the conversion of DHA to LA (conditions: 80 mg SnP-PEG2000, 140 °C).
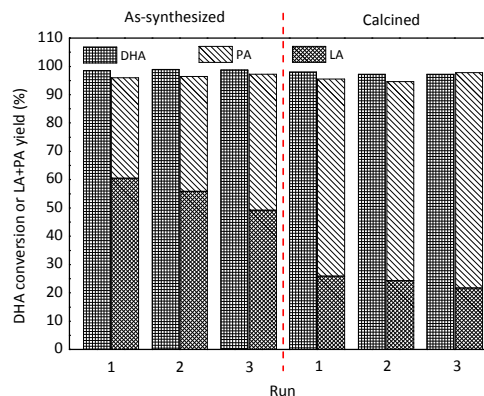

Fig. 9 Results of reuse study. (Conditions: 0.3125 M DHA, 80 mg SnP-PEG2000, 140 °C, 1 h).

significantly affected the LA yield. The yield of LA increased significantly with the increase in the temperature between 120 °C and 160 °C. Moreover, the maximum LA yield increased with increasing reaction temperature, and the highest LA yield was observed (96.3%) at 160 °C. The higher the temperature was, the shorter the reaction time needed to obtain the optimum yield. It has been shown that the reaction rate increased significantly at high temperatures in the initial stages of reaction. The colour of the product was pale yellow, which was an indication that a significant amount of black humin oligomer did not form under these conditions. With the increase in temperature, the colour of the reaction solution changed from yellow to dark brown. This change of colour was caused by the formation of various polycondensation products.[11]

The effect of SnP-PEG2000 dosages on the conversion of DHA and the yield of LA is presented in Fig. 7. Evidently, higher catalyst concentrations led to higher reaction rates. At the same reaction time, both the DHA conversion and the yield of LA were higher when higher catalyst dosages were utilized. Moreover, higher final LA yields were observed with higher catalyst concentrations.

The effect of the initial DHA concentration on the DHA conversion and LA yield is presented in Fig. 8. The DHA conversion was independent of the initial concentration of DHA, which is an indication that the reaction was first order with regard to DHA. However, the yield of LA was a function of the initial concentration of DHA and was significantly higher when a low initial substrate concentration was utilized. The formation of brown soluble materials was more frequently observed when high initial concentrations of DHA were utilized.[16]

Catalyst recyclability

To verify the stability of the catalyst, three consecutive reactions were run with both the as-synthesized and calcined SnP-PEG2000 materials. Between runs the catalyst was dried at 60 °C or calcined at 550 °C and weighed before the next run,

in order to maintain a constant substrate-to-catalyst ratio. Results of the reuse study are shown in Fig. 9. The as-synthesized catalyst proved to be recyclable, as complete DHA conversion was observed without significant loss of LA yield. The slight decrease in LA yield could be ascribed to the partial decomposition of PEG2000 or the intensive formation of humins during the reaction. The carbon deposition could be inferred from the increased weight loss ratio of the recycled catalysts (Table S4). Moreover, ICP analysis showed a loss of less than 1% of the initial Sn content. No sign of loss in the total yield of PA and LA was observed. PEG possessed excellent stability in the highly acidic media, indicating that it was beneficial in the production of LA in the current acidic system.[43] The FTIR spectra of the as-synthesized SnP-PEG2000 confirm that the catalyst was stable after three consecutive runs (Fig. 1). Only slightly lowered BET surface area and total acid sites were observed after each cycle (Table S4). The UV-vis DRS spectra shows that SnO_2 is formed after the 3rd cycle, possibly due to the partial hydrolysis of SnP (Fig. 2b). Meanwhile, the calcined material was also proved to be recyclable though low LA yields were observed. Furthermore, the as-synthesized SnP-PEG2000 was treated in water without reactants under reaction conditions. The separated two phases were then used separately for the conversion of DHA at 140 °C for 6 h. The "washed" solid phase afforded a DHA conversion of 99% for a LA yield of 95.2%, while the "solid-free" liquid phase alone resulted in a conversion of 88.8% for a LA yield of 0.46%. The heterogeneous catalytic activity can thus be demonstrated by these regeneration tests. This outcome demonstrates the recyclability of SnP-PEG2000 and its potential for use during the conversion of carbohydrates.

Proposed mechanism

The catalytic effects of the SnP-PEG2000 materials were observed for both the overall reaction of DHA to LA (Fig. 5a) and the conversion of PA to LA (Table 3). It was likely that the tin species acted as Lewis acid sites and that they accelerated the keto-enol tautomerization of DHA and subsequent dehydration by coordination to the carbonyl and hydroxyl groups to form PA.[12] Moreover, the conversion of DHA to PA was also catalyzed by H+, as shown for the reaction of DHA using phosphoric acid (Table 2, entry 2).

It was proposed that the isomerization of the intermediate PA to LA involves a Meerwein-Ponndorf-Verley reduction and Oppenauer oxidation (MPVO)-type redox step that is catalyzed only by Lewis acids.[17] This seems rational when considering that a conversion as high as 49.3% was observed when PA was catalyzed by phosphoric acid and only a trace amount of LA was obtained (Table 3, entry 2). Previously, the dehydration of DHA to PA was demonstrated to be the rate-determining step in other systems.[18] However, in the present study, the reaction network appeared to be dominated by the rehydration and isomerization of PA to LA. The concentration of PA was observed to be the highest at very short reaction times for both DHA and GLA (Fig. 5). Then, the yield of LA increased significantly with the diminishing of PA, indicating a lower
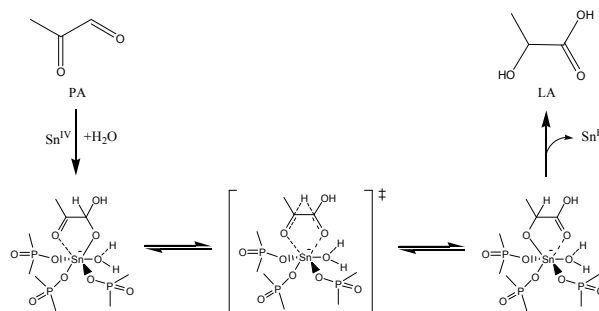
Scheme 2 Proposed reaction mechanism for the conversion of PA to LA.
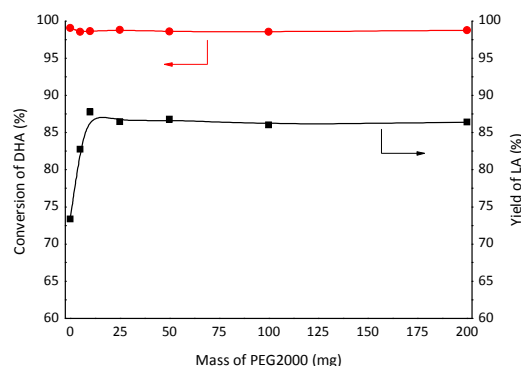

Fig. 10 Effect of the mass of PEG2000 on the conversion of DHA to LA (conditions: 0.3125 M DHA, 80 mg SnP, 140 °C, 4 h).

reaction rate of PA than DHA. The total acid sites of SnPs are almost one order of magnitude larger than that of hydrothermal Sn-Beta (0.083 mmol g^{-1}), efficiently facilitating the dehydration and rearrangement of DHA.[18] Besides, the large increase of Brønsted acid sites after surfactant loading accords to acceleration of the dehydration reaction. It's worthwhile to mention that the proper ratio of Brønsted to Lewis acid sites makes SnP-PEG2000 an efficient catalyst, thus getting rid of the formation of undesirable acetal byproduct from PA.[44]

In addition, $SnCl_4 \cdot 5H_2O$ as well as nanopowdered SnO_2 afforded LA selectivities below 7% from the conversion of DHA, illustrating that when tin is incorporated into the SnP framework it becomes more active for the formation of LA (Table 2, entries 3, 14). The catalytically active site is supposed to be a partially hydrolyzed framework tin species, which is also believed to be the active site of Sn-Beta.[17] The rate-determining step involves a MPVO-type redox reaction of the hydrted PA in which a 1, 2-hydride shift takes place in a concerted fashion (Scheme 2).

The role of surfactants

To confirm the effect of the surfactants, a varying amount of PEG2000 was added to the non-surfactant SnP catalyzed reaction system, and the results are presented in Fig. 10. In the

absence of PEG2000, a relatively low yield was obtained (73.4%). The yield of LA increased with the addition of incremental PEG2000, and an excellent yield was obtained when the amount of PEG2000 reached 10 mg (87.8%). However, a slight decrease in the LA yield was observed when the amount of PEG2000 was further increased, and the final yield was 86.4%. The results indicate that the addition of a proper amount of PEG2000 significantly promotes the catalytic efficiency of the current system, even though the optimum yield of LA was still lower than that catalyzed by the SnP-PEG2000 materials (87.8% vs. 96.1%). However, hardly any increase in LA yield could be obtained when PEG2000 was added to the Sn-Beta catalyzed system, possibly due to the significantly lower acid density of Sn-Beta (Table S5). In addition, the efficiency of the various chain length PEGs in the reaction was also examined under the same reaction conditions (Fig. 11). The average molecular weight had a limited impact on the yields of LA, and PEG2000 was slightly superior to the other PEGs investigated. It should be noted that only a trace amount of the desired product was formed using neat PEG2000 as the catalyst (LA yield of 0.8%), indicating that the active sites of the tin phosphates were not directly introduced by the surfactant.

A possible mechanism, which seems to be attributed to the properties of PEG2000 as the phase transfer catalyst, involves the fact that PEG2000 is prone to form complexes with metal cations similar to crown ethers during the synthesis of tin phosphates.[45] The metal cations were bound to the polymer ligand by the coordinate bonds (electrostatic attraction) because the polymer ligand contained plenty of anchoring site-electronegative oxygen atoms.[46] The coordination between the PEG2000 and the metal cations caused a greater separation of the tin ions from the phosphate anions, making the tin ions into more potent Lewis acid sites.[42, 47] In addition, the XPS analysis corroborated this hypothesis (see Fig. 2a), as it demonstrated a higher polarity of Sn^{IV} of the as-synthesized SnP-PEG2000 compared to the calcined one. During the reaction, the acyclic polyethers tended to attract the organic reactants to the surface of catalysts because of their lipophilicity. Therefore, a local
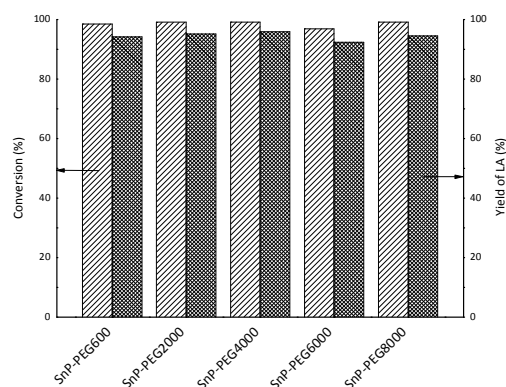

Fig. 11 Effect of the chain length of PEG on the conversion of DHA to LA (conditions: 0.3125 M DHA, 80 mg Catalyst, 140 °C, 4 h).

organic phase was formed on the surface of the catalyst and the complexes tended to decompose to expose the active metal sites to catalyze the reaction (as shown in Scheme 3). It's worthwhile to mention that the PVP modified SnP could also result in a promising final LA yield (92%) under consistent reaction conditions. Indeed, polymer-supported catalysts, which were developed based on the microencapsulation technique for binding catalysts to polymers, have created highly active heterogeneous metal catalysts for many useful organic reactions.[48] Detailed characterization including ^{119}Sn MAS NMR is in progress to test the Sn complexation by PEG2000.

To further confirm the role of the phase transfer catalysts, several commonly used phase transfer catalysts, such as CD, TBAB, and CTAB, were also used during the synthesis of tin phosphates. SnP-CD resulted in an efficient catalytic performance because CD had an intrinsic hydrophobic cavity to encapsulate metal cations and reactants. The high efficiency of TBAB encouraged us to propose that the coordination
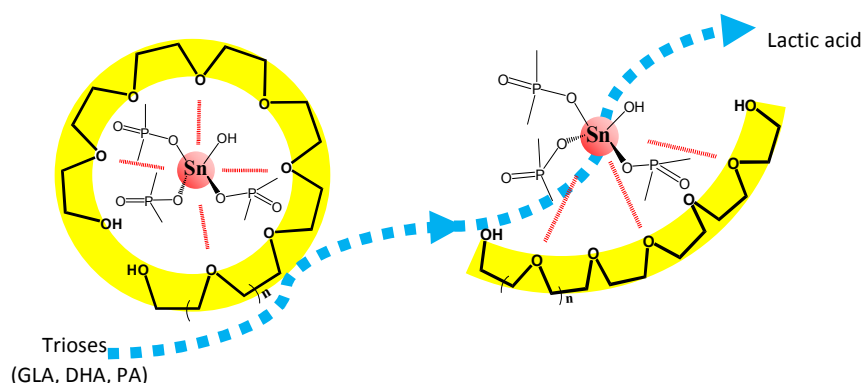
Scheme 3 Postulated roles of SnP-PEG2000 during the conversion of DHA into LA. ● Active sites; ⌇ PEG2000; ⋰ Trioses (The catalytic active sites were covered by PEG2000 in the aqueous phase (left) and then exposed (right) due to the formation of local organic phase). A schematic diagram was used to explain the exposure of the active metal sites (Scheme S1).

between surfactants and the anionic parts of the solid acid catalysts was also beneficial for the catalytic activity. Thus, an efficient surfactant for the synthesis of tin phosphates with high catalytic activity for the conversion of sugars to LA was supposed to meet the following criteria: 1) the coordination ability between surfactants and metal cations or anionic groups of the solid acid catalysts, 2) the formation of microenvironment during the reaction and 3) good solubility in organic phase. The detrimental effect of CTAB might arise from its long alkyl chains which were supposed to hinder the coordination. These findings indicate that types of phase transfer catalysts other than acyclic polyethers might also be introduced to the current reaction system, thereby broadening the scope of phase transfer catalysts to the conversion of carbohydrates. When non-phase transfer catalyst (IMEP) was used, poor catalytic activity was observed (Table 2, entry 5). Considering the fact that PEG is economically available and environmentally friendly, the findings of this study created a foundation for the potential commercial application of PEG for the production of LA.

Conclusions

This work presented a preliminary study on the feasibility of the use of surfactants modified tin phosphates as phase transfer catalysts for the isomerization of trioses (DHA and GLA) to LA. The product distribution was closely related to the substrate concentrations, reaction temperatures, catalyst loading, and reaction times. Under the optimized reaction conditions, an almost quantitative yield (96%) of LA was obtained by using SnP-PEG2000. A possible reaction mechanism involving the concept of phase transfer catalysis was proposed. These results not only broaden the scope of phase transfer catalysts but also encourage the use of tin phosphates modified with surfactants as new solid acid catalysts for the conversion of carbohydrates. This protocol will serve as an efficient and green method for the production of LA. Currently, further efforts to extend the application of the system to other solid acid catalyzed transformations of carbohydrates are ongoing in our laboratory.

Experimental

Materials and instrumentation

Poly(ethylene glycol) (PEG), poly(ethylene glycol) dimethyl ether (NHD, 99%), and cyclodextrin (CD, 98+%) were purchased from Aladdin Chemistry Reagent Company (Shanghai, China). 1, 3-dihydroxyacetone (DHA, 98%), tin chloride (99%), phosphoric acid (85+%), tetrabutyl ammonium bromide (TBAB, 99%), pyruvaldehyde (PA, 40 wt% solution in water) and hexadecyl trimethyl ammonium bromide (CTAB, 99%) were purchased from J&K Scientific Ltd. (Beijing, China). Pluronic P123, pluronic F127, and glyceraldehyde (GLA) was purchased from Sigma-Aldrich USA. A 1.0 N standardized LA solution (Alfa Aesar Company) was used during the quantitative

analysis of LA. All reagents were used as received. Polymerizates of imidazole and epichlorohydrin (IMEP) was synthesized following the procedure previously reported.[47]

Structural information on the as-synthesized and calcined tin phosphate materials was obtained by powder X-ray diffraction (PXRD) (D8FOCUS, Bruker), X-ray photoelectron spectroscopy (XPS) (ESCALAB-250, ThermoFisher Scientific), Fourier transform infrared spectroscopy (FTIR) (TENSOR 27, Bruker), Brunauer-Emmett-Teller (BET) surface area measurements (SORPTOMATIC 1990, Thermo Electron Corporation), Solid-state ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) (AV300, Bruker), and transmission electron microscopy (TEM) (JEM-3010, JEOL). The amounts of tin and phosphorus present in the solid acid catalysts were determined by elemental analysis through inductively coupled plasma (ICP) analysis. The coordination of tin species was examined by UV-vis diffuse reflectance spectroscopy (DRS). Spectra were recorded on a Shimadzu UV-3600 spectrophotometer using $BaSO_4$ as reference. SnO_2 was measured after calcination at 550 °C. Total acid sites were determined by temperature-programmed desorption of ammonia (NH_3-TPD) (OmniStar, MS200). Analysis of Brønsted and Lewis acidity was carried out by pyridine probe FTIR spectroscopy.

Catalysts preparation

SnP was synthesized with varying surfactants using procedures analogous to those reported by Dutta et al.[26] In a typical process, certain amounts of H_3PO_4 and PEG2000 (2 g) were dissolved in water (90 mL), and this mixture was stirred for 2 h. A certain amount of tin tetrachloride dissolved in water (60 mL) was added drop-wise to the aforementioned stirred aqueous solution. The resulting white colloidal precipitate was stirred for another 3 h. It was then filtered, washed with demineralized water and dried at room temperature. Finally, part of the material was calcined at 550 °C for 6 h. The obtained material was designated SnP-PEG2000, where PEG2000 refers to the surfactant utilized in the process.

To compare the catalytic activities, a large-pore mesoporous SnP was synthesized according to Dutta et al.[26] Sn-Beta was also synthesized according to a previously published procedure.[34]

General procedure for the conversion of DHA to LA

Aqueous solutions of DHA were prepared by dissolving dimeric DHA in deionized water. The DHA dimers dissociated into the monomeric form in the aqueous solution. Batch reactions were conducted in a sealed vial (15 mL capacity) placed in a temperature-controlled oil bath. Throughout all the experiments, the amount of the loaded reaction solution was kept constant at 4 mL. Temperatures in the reactor were measured by a thermocouple in contact with the solution. All reaction solutions were mixed at a maximum constant rate of 500 rpm using an internal stirrer. The samples were

immediately quenched in an ice water bath, centrifuged and then filtered with a 0.2 μm syringe filter prior to analysis.

The concentrations of the reactants and product samples were analyzed by HPLC (Agilent 1200, USA) using a Biorad Aminex HPX-87H column at 35 °C with 0.005 M H_2SO_4 eluent at a flow rate of 0.5 mL/min. A Refractive Index Detector was employed. A typical chromatogram for the conversion of GLA into LA is presented in Fig. S5.

The conversion of DHA and the yield of LA were determined based on the amount of carbon.[50] The experiments were replicated at least three times and were reported as the mean values. The error was below 5%.

Acknowledgements

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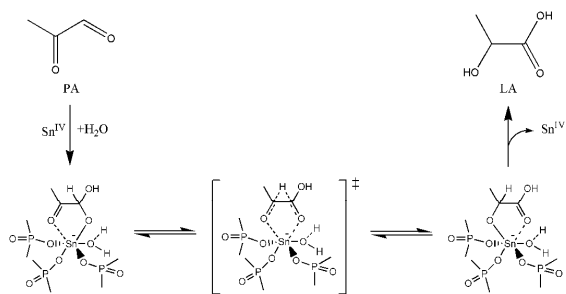
Tin phosphate phase transfer catalysts were used efficiently for the conversion of trioses to lactic acid under hydrothermal conditions.