Supporting Information

Catalysis Science & Technology

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

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Table S1 Catalytic conversion of GLA to LA by tin materials with various surfactants. ($[GLA]_o$=0.3125 M; Catalyst=80 mg; T= 140 °C; t=15 min).

Entry	Catalyst	As-synthesized				Calcined			
		GLA Conv. (%)	DHA (%)	PA (%)	LA (%)	GLA Conv. (%)	DHA (%)	PA (%)	LA (%)
1	Blank	75.88	14.12	4.39	3.27	-	-	-	-
2	H_3PO_4	54.86	4.62	47.71	2.52	-	-	-	-
3	$SnCl_4 \cdot 5H_2O$	90.17	22.40	64.23	3.54	-	-	-	-
4	SnP	91.12	15.26	64.71	11.15	74.49	20.93	46.75	6.81
5	SnP-IMEP	83.63	24.43	49.63	9.57	86.74	20.70	58.37	7.67
6	SnP-P123	98.14	4.24	69.25	24.65	91.85	17.45	63.76	10.64
7	SnP-P123[a]	98.53	3.65	68.14	24.32	90.91	17.52	64.31	9.58
8	SnP-F127	97.95	5.89	69.24	22.82	84.65	22.35	56.60	5.71
9	SnP-PEG2000	95.48	11.70	66.46	17.33	67.61	20.91	41.66	5.04
10	SnP-NHD	95.79	9.07	70.11	16.61	66.11	27.28	31.85	6.98
11	SnP-CD	93.79	12.01	67.58	14.20	84.01	23.72	50.36	9.93
12	SnP-TBAB	95.45	8.30	69.56	17.59	79.52	19.62	51.25	8.65
13	SnP-CTAB	95.48	14.77	60.17	20.54	96.81	9.03	68.89	18.89
14	SnO_2	-	-	-	-	87.98	23.01	2.60	4.24
15	Sn-Beta	-	-	-	-	65.52	34.80	17.44	3.02

[a] Large-pore mesoporous SnP.

Table S2 Initial rates of reaction using tin materials with various surfactants.

($[DHA]_o$=0.3125 M; Catalyst=80 mg; T= 140 °C).

Entry	Catalyst	As-synthesized			Calcined		
		DHA	PA	LA	DHA	PA	LA
1	Blank	13	6	6	-	-	-
2	H_3PO_4	267	214	11	-	-	-
3	$SnCl_4 \cdot 5H_2O$	290	228	46	-	-	-
4	SnP	530	410	86	489	366	73
5	SnP-IMEP	493	375	82	560	441	82
6	SnP-P123	786	567	177	696	530	127
7	SnP-P123[a]	799	551	183	713	511	127
8	SnP-F127	728	542	147	570	443	87
9	SnP-PEG2000	725	539	148	341	258	56
10	SnP-NHD	808	572	197	332	247	60
11	SnP-CD	766	555	173	499	385	81
12	SnP-TBAB	686	514	133	456	343	80
13	SnP-CTAB	453	342	76	705	535	128
14	SnO_2	-	-	-	65	36	22
15	Sn-Beta	-	-	-	375	71	165

[a] Large-pore mesoporous SnP, Data are given in units of [$\mu mol\ g_{cat}^{-1}\ min^{-1}$].

Table S3 Initial rates of reaction using tin materials with various surfactants.

([PA]$_o$=0.3125 M; Catalyst=80 mg; T= 140 °C).

Entry	Catalyst	As-synthesized		Calcined	
		PA	LA	PA	LA
1	Blank	27	8	-	-
2	H_3PO_4	23	10	-	-
3	$SnCl_4{\cdot}5H_2O$	231	125	-	-
4	SnP	171	136	227	114
5	SnP-IMEP	224	156	217	140
6	SnP-P123	225	134	183	134
7	SnP-P123[a]	223	134	193	139
8	SnP-F127	327	262	220	131
9	SnP-PEG2000	259	213	106	65
10	SnP-NHD	290	227	160	74
11	SnP-CD	261	215	241	142
12	SnP-TBAB	118	109	222	108
13	SnP-CTAB	314	239	299	230
14	SnO_2	-	-	70	22
15	Sn-Beta	-	-	613	589

[a] Large-pore mesoporous SnP, Data are given in units of [μmol g_{cat}^{-1} min^{-1}].

Table S4 Characterization of the recycled SnP-PEG2000 by adsorption and TGA analysis.

SnP-PEG2000	Run	BET surface area (m^2 g^{-1})	Total acid sites (mmol g^{-1})	Weight loss (%)	Carbon deposition (%)
As-synthesized	1	165.3	1.36	8.6	-
	2	162.5	1.33	9	0.4
	3	160.3	1.3	9.3	0.7
Calcined	1	290.3	0.83	3.5	-
	2	285.6	0.8	4.8	1.3
	3	283.8	0.79	5	1.5

Table S5 Conversion of DHA to LA catalyzed by Sn-Beta with additional PEG2000.

([DHA]$_o$=0.3125 M; Sn-Beta=80 mg; T= 140 °C; time=4 h).

Entry	PEG2000 (mg)	DHA Conv. (%)	LA (%)
1	0	98.0	91.3
2	5	97.5	92.6
3	10	97.8	91.7
4	15	98.1	93.1
5	20	96.9	92.4

Table S6 Catalytic conversion of DHA to LA by tin materials with various surfactants. ($[DHA]_o$=0.3125 M; Catalyst=80 mg; T= 140 °C; t=15 min).

Entry	Catalyst	As-synthesized			Calcined		
		DHA Conv. (%)	PA Yield (%)	LA Yield (%)	DHA Conv. (%)	PA Yield (%)	LA Yield (%)
1	SnP	57.2	46.8	8.8	52.8	41.7	7.5
2	SnP-IMEP	53.1	42.7	8.4	60.4	50.2	8.4
3	SnP-P123	84.8	64.5	18.2	75.1	60.3	12.9
4	SnP-P123[a]	86.2	62.8	18.7	76.9	58.3	13.1
5	SnP-F127	78.6	61.7	15.1	61.5	50.5	8.9
6	SnP-PEG2000	78.3	61.4	15.2	36.8	29.4	5.8
7	SnP-NHD	87.2	65.2	20.3	35.8	28.1	6.2
8	SnP-CD	82.2	62.9	17.3	53.9	43.9	8.3
9	SnP-TBAB	73.9	58.6	13.6	49.2	39.1	8.2
10	SnP-CTAB	48.9	38.9	7.8	76.1	60.9	13.1
11	Sn-Beta	-	-	-	23.2	4.1	13.6

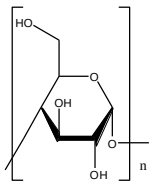
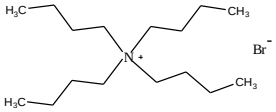
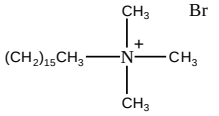
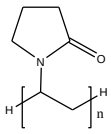
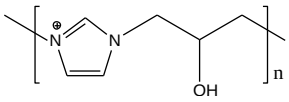
[a] Large-pore mesoporous SnP.

Table S7 Catalytic conversion of DHA to LA by 20 mg SnP-PEG2000 over prolonged reaction times. ($[DHA]_o$=0.3125 M; T= 140 °C).

Entry	Time (h)	DHA Conv. (%)	LA Yield (%)
1	8	>99	55.9
2	10	>99	56.7
3	12	>99	57.1

In order to further investigate the increasing trend of LA yields when 20 mg catalysts were used, further experiments were conducted under similar reaction conditions and results are shown in Table S4. The yield of LA increased only slightly at prolonged reaction times and plateaued at 57%. One possible explanation is that the formation of LA over long reaction times resulted in a strong Brønsted acid environment, facilitating the conversion of PA to undesirable byproducts when the catalyst loading was low.

Table S8 Formula or structure of the surfactants.

Entry	Surfactant	Formula or Structure
1	P123	$PEO_{20}PPO_{70}PEO_{20}$
2	F127	$PEO_{106}PPO_{70}PEO_{106}$
3	PEG	$HO\text{-}(CH_2CH_2O)n\text{-}H$
4	NHD	$H_3CO\text{-}(CH_2CH_2O)n\text{-}CH_3$
5	CD	
6	TBAB	
7	CTAB	
8	PVP	
9	IMEP	

PEO: $-(CH_2CH_2O)n-$; PPO: $-(CH_2CH_2CH_2O)n-$

Table S9 Charaterization of the tin materials with various surfactants by adsorption.

		As-synthesized		Calcined	
Entry	Catalyst	BET surface area ($m^2\ g^{-1}$)	Total acid sites ($mmol\ g^{-1}$)[b]	BET surface area ($m^2\ g^{-1}$)	Total acid sites ($mmol\ g^{-1}$)[b]
1	SnP	146	0.75	168	0.67
2	SnP-IMEP	121	0.82	235	0.71
3	SnP-P123	137	1.09	196	1.12
4	SnP-P123[a]	149	1.28	218.	1.19
5	SnP-F127	132	1.33	162	1.03
6	SnP-PEG2000	170	1.39	287	0.82
7	SnP-NHD	175	1.25	215	0.75
8	SnP-CD	158	1.17	221	0.87
9	SnP-TBAB	139	1.31	183	0.92
10	SnP-CTAB	123	0.94	265	0.73

[a] Large-pore mesoporous SnP, [b] Determined from ammonia TPD.

Table S10 Solubility studies of SnP-PEG2000 in water/surfactant mixtures.

SnP-PEG2000	Water (mL)	Surfactant (mg)	Weight loss (wt %)
	8	0	0.7
	8	5	1.3
As-synthesized	8	10	1.0
	8	20	0.9
	8	30	0.6
	8	0	0.9
	8	5	1.1
Calcined	8	10	1.3
	8	20	0.8
	8	30	0.7

The solubility test of the SnP-PEG2000 (with and without calcination) was performed in water and water/surfactant mixtures. 500 mg of the materials were added to 8 mL water or surfactant solutions with varying mass. Then the mixture was subjected to filtration after magnetic stirring for 4 h and the wet filter paper was put in vacuum oven overnight. Both the weight of the filter paper and the dried weight of filter plus catalysts were measured during the period. The residue was obtained in this way and the mass loss was then calculated (Table S9).

A slight weight loss (approximately 1%) was observed when the as-synthesized SnP-PEG2000 was recovered from pure water or water/surfactant mixtures. A decreased mass loss ratio was obtained with the addition of incremental PEG2000, indicating the deposition of surfactant on the catalyst surface. A similar trend was observed with the calcined materials. The weight loss could be considered as an overall effect of 1) inevitable loss during filtration, 2) catalyst dissolution and 3) dissolution or deposition of surfactants. It is tough work to study the effect of each factor; however, the deposition of surfactants could be excluded because the current system did not need additional surfactants. Moreover, the SnP exhibited high hydrolytic stability in acid media; this is beneficial for the current acid catalyzed reaction.[S1]

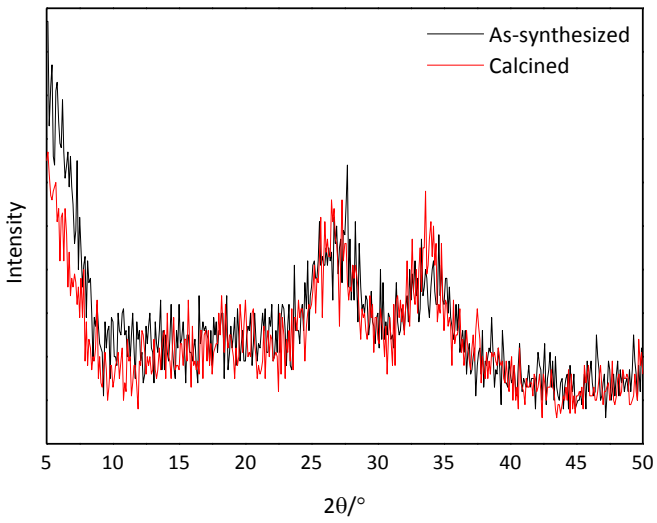


Fig. S1 Wide angle PXRD pattern for the as-synthesized and calcined SnP-PEG2000.

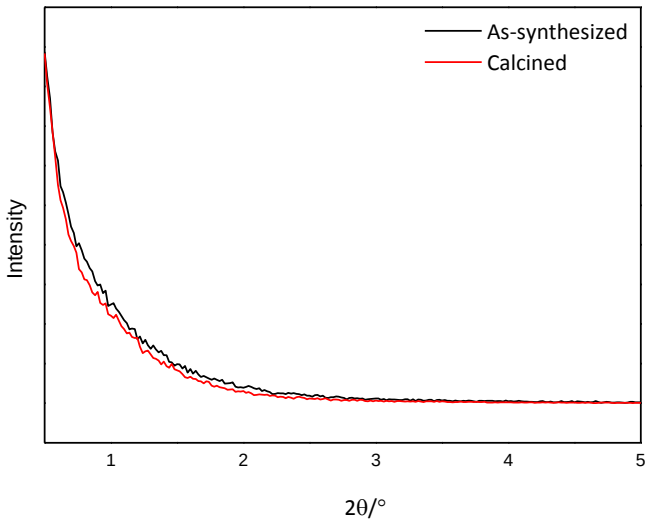


Fig. S2 Small angle PXRD pattern for the as-synthesized and calcined SnP-PEG2000.

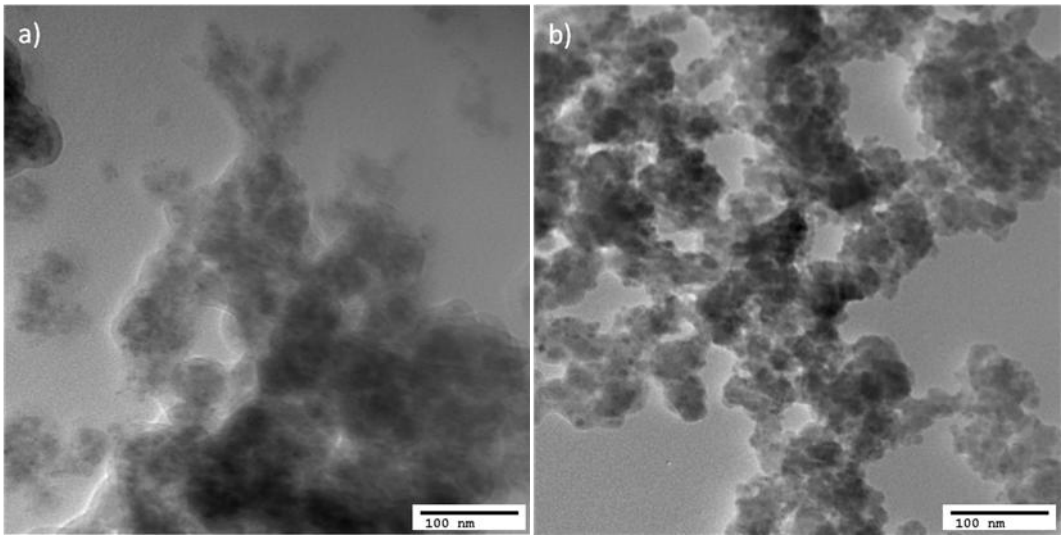


Fig. S3 TEM images of the a) as-synthesized and b) calcined SnP-PEG2000.

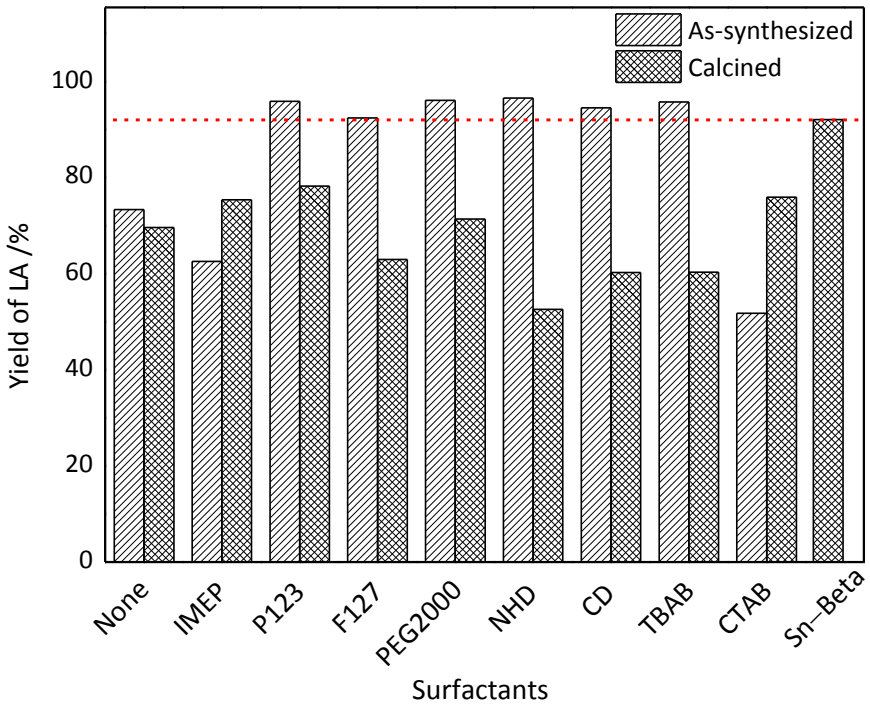


Fig. S4 The results of DHA conversion after a prolonged reaction time of 6 h (Conditions: 0.3125 M DHA, 80 mg SnP Catalyst, 140 °C, 6 h). Sn-Beta, which is one of the state-of-the-art catalysts, was used as a reference.

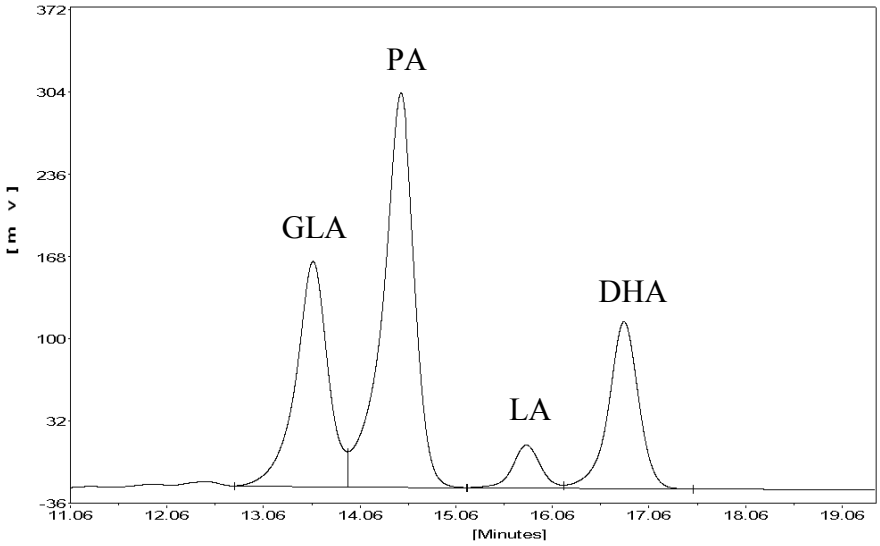


Fig. S5 HPLC chromatogram of the aqueous phase obtained from the hydrothermal treatment of GLA (conditions: 0.3125 M GLA, 80 mg SnP-PEG2000, 140 °C; reaction time: 5 min).

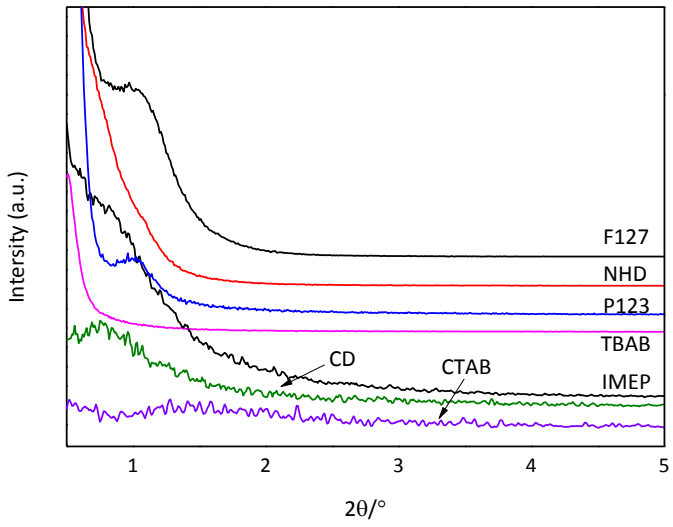


Fig. S6 Small angle PXRD pattern for the calcined SnP with varying surfactants.

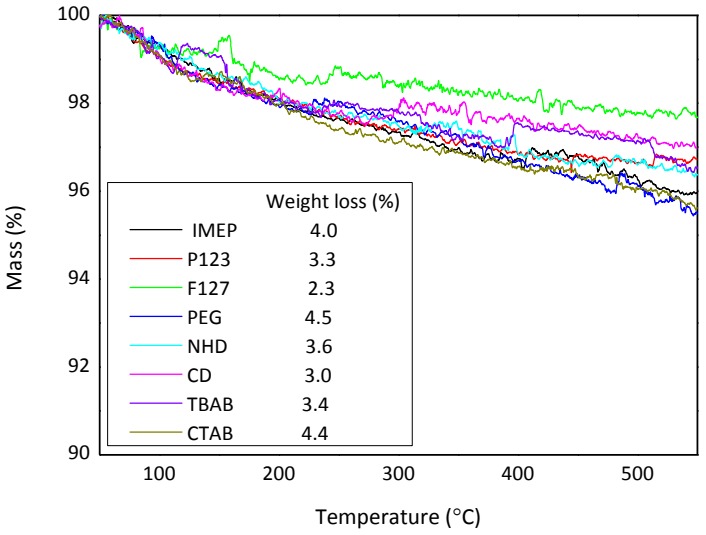


Fig. S7 TGA of calcined SnP with surfactants and corresponding weight loss ratio.

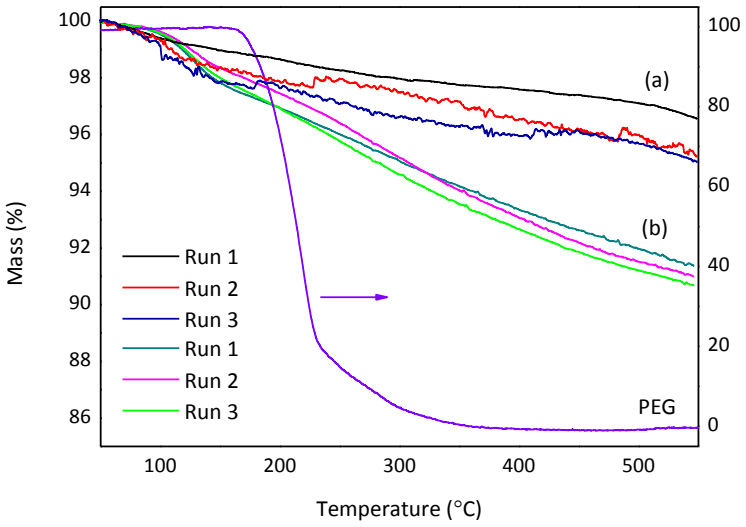
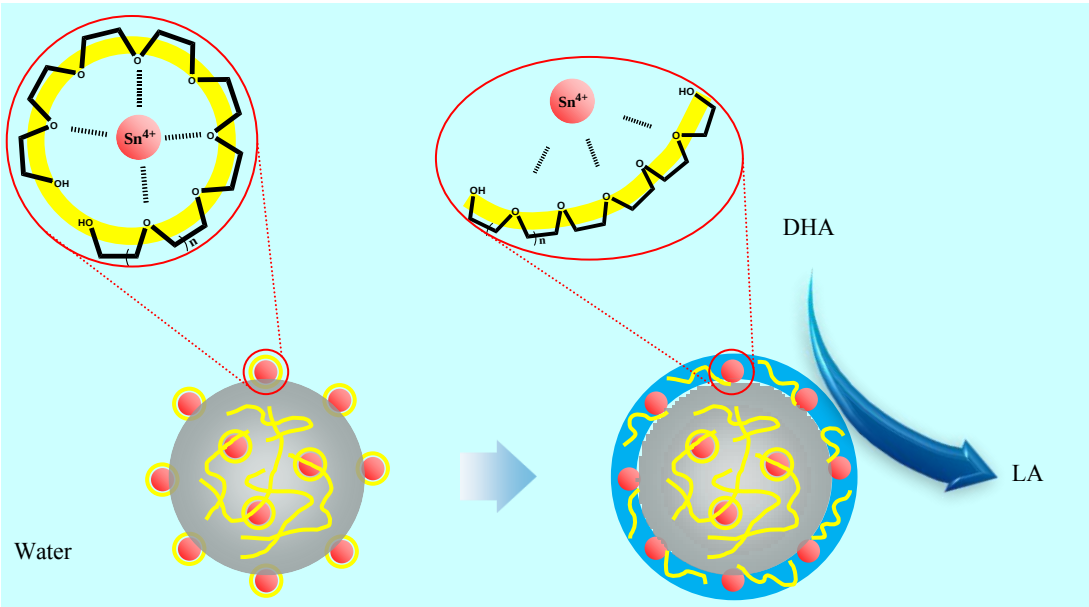


Fig. S8 TGA analysis of the calcined (a) and as-synthesized (b) SnP-PEG2000 and PEG 2000 during three consecutive runs.

The TGA analysis diagram can be divided into two regions in the temperature range from 50 to 550 °C, the first is between 50 and 130 °C, the second between 130 and 550 °C, as shown in Fig. S8. The first region was attributed to the removal of physically bound water. The second weight loss mainly resulted from the structural water release due to the partial condensation of HPO_4 groups. From the TGA spectrum of PEG, it was obvious that the decomposition of PEG was included in the second region from 170 to 400 °C. A slightly increased mass loss ratio was obtained, possibly due to the deposition of carbon during the reaction.[S1] The polymer content of SnP-PEG2000 was approximately 4% (Table S8).



Scheme S1 Postulated roles of SnP-PEG2000 during the conversion of DHA into LA. Solid catalyst; Active sites; PEG2000; Organic membrane.

References

S1. A. I. Bortun, S. A. Khainakov, L. N. Bortun, E. Jaimez, J. R. García and A. Clearfield, *Mater Res Bull*, 1999, 34, 921-932.