

An efficient and durable catalyst of hierarchically porous KLA/TiPO for vapor phase condensation of lactic acid to 2,3-pentanedione

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Catalyst characterization

Powder X-ray diffraction (XRD) measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-K α radiation. The FTIR spectra of the catalysts were recorded in the range of 500-4000 cm⁻¹ on a Nicolet 6700 spectrometer. The specific surface areas of catalysts were measured through nitrogen adsorption at 77 K using TriStar II 3020 instrument. Prior to adsorption, the samples were treated at 250 °C under vacuum for 6 h and the specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. Surface acid and base properties of the samples were estimated by NH₃-TPD and CO₂-TPD, respectively, on a Finesorb-3010 Instrument. The sample (ca. 50-60 mg) was purged with dry Ar (50 mL/min, purity > 99.999 v/v%) at 300°C for 1.0 h, followed by reducing the furnace temperature to room temperature, and switching to a flow of 8 v/v% NH₃/He or 10 v/v% CO₂/He for 1 h to execute NH₃ or CO₂ adsorption. Next, the samples were swept by dry Ar (50 mL/min, purity > 99.999 v/v%) at 80°C for 1.0 h to remove the dissociative NH₃ or CO₂ on the surface of

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samples. Then, NH₃ or CO₂ chemically adsorbed on the sample is desorbed in the range of 80-650°C at a rate of 10 °C/min.

Activity evaluation

The condensation of lactic acid to 2,3-pentanedione over the catalysts was carried out in a vertical fixed-bed quartz tubular reactor with a 4 mm inner diameter operated at atmospheric pressure. The catalyst (ca. 0.30-0.40 g, 20-40 meshes) was placed in the middle of the reactor and quartz wool was placed in both ends. Firstly, the catalyst was pretreated at the required reaction temperature (ca. 270 °C) for 1.0 h under N₂ with high purity (0.1 MPa, 1.2 mL/min). The feedstock (20 wt% aqueous solution of LA) was then pumped into the reactor (LA aqueous solution flow rate, 1.0 mL/h) and driven through the catalyst bed by nitrogen. The liquid products were condensed using ice-water bath and analyzed offline using SP-6890 gas chromatograph (GC) with a FFAP capillary column connected to a FID. Quantitative analysis of the products was carried out by the internal standard method using isopropanol as the internal standard material. GC-MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment. The reaction tail gas was analyzed online using GC with a packed column of TDX-01 connected to TCD detector. The conversion of LA and the selectivity toward 2,3-pentanedione or other by-products were calculated according to equations (1) and (2).

$$\text{Conversion / \%} = \frac{n_0 - n_1}{n_0} \times 100 \text{----- (1)}, \quad \text{Selectivity / \%} = \frac{n_p}{n_0 - n_1} \times 100 \text{----- (2)}$$

Where n_0 is the molar quantity of LA fed into reactor, n_1 is the molar quantity of LA in the effluent, and n_p is the molar quantity of lactic acid converted to 2,3-pentanedione or other byproducts such as acetaldehyde, propionic acid, acrylic acid, and acetic acid.

According to previous references^{1, 2}, LA consumption rate and 2,3-PD formation rate are defined as follows with equations (3) and (4).

$$\text{LA consumption rate} = \frac{\text{amount of LA consumed per hour in the reactor (mmol/h)}}{\text{surface area of catalyst in the reactor (m}^2\text{)}} \text{-----(3)}$$

$$\text{2, 3 - PD formation rate} = \frac{\text{amount of 2,3-PD formed per hour in the reactor (mmol/h)}}{\text{surface area of catalyst in the reactor (m}^2\text{)}} \text{-----(4)}$$

Tables

Table S1 NH₃(CO₂)-TPD of catalysts

Samples	Peak area CO ₂ -TPD(x10 ⁵)	Peak area NH ₃ -TPD(x10 ⁵)
6:1	1.39	1.17
5:1	1.49	1.30
4:1	1.56	1.30
3:1	1.42	1.37
2:1	1.38	1.28
1:1	1.05	1.19
1:0.5	0.46	0.49
Ti ₃ (PO ₄) ₄	--	--

Table S2 Effect of LA concentration

LA Concentration(wt%)	LA Conv. (%)	Sel.(%)				
		2,3-PD	AD	PA	AC	AA
10	82.3	58.0	5.2	12.1	5.8	18.1
20	85.7	69.0	3.9	13.1	2.2	11.1
30	86.3	77.2	3.3	9.2	1.4	6.1
40	88.9	79.8	3.1	10.1	1.1	4.7
50	71.2	81.4	1.7	10.1	1.5	4.2
60	65.7	83.6	1.5	7.2	1.5	4.1

a: KNO₃/TiPO catalyst with KNO₃ : TiPO = 4:1, 0.38 mL, 0.30 g; particle size: 20-40 meshes; carrier gas N₂: 1.2 mL/min; LA feed flow rate: 1.0 g/h; reaction temp.: 270°C; TOS: 7-8 h. b: LA: lactic acid, 2,3-PD: 2,3-pentanedione, AD: acetaldehyde, AC: acetic acid, PA: propionic acid, AA: acrylic acid. c: Mass balance > 90%.

Table S3 Effect of reaction temperature

Reaction temp.(°C)	LA (%)	Conv.	Sel.(%)				
			2,3-PD	AD	AC	PA	AA
250	65.5		75.4	2.9	2.1	7.1	7.0
260	80.2		74.8	3.7	1.1	8.2	7.5
270	87.5		72.7	3.8	1.8	10.2	11.1
280	90.7		70.7	3.9	1.4	12.8	10.6

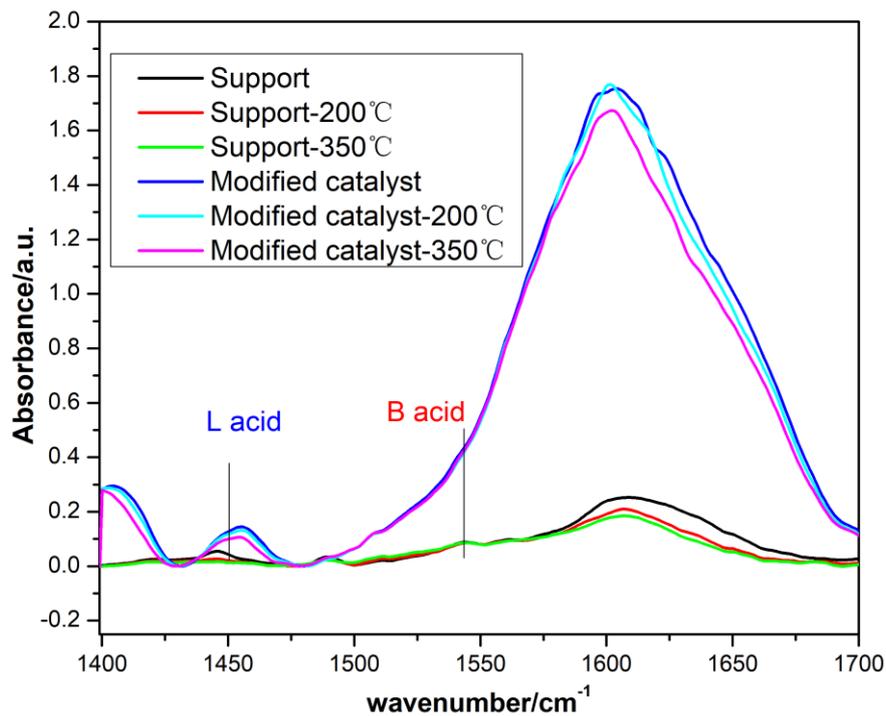
a: KNO₃/TiPO catalyst with KNO₃ : TiPO = 5:1, 0.38 mL, 0.30 g; particle size: 20-40 meshes; carrier gas N₂: 1.2 mL/min; LA feedstock: 20 wt% in water, LA feed flow rate: 1.0 g/h; TOS: 7-8 h. b: LA: lactic acid, 2,3-PD: 2,3-pentanedione, AD: acetaldehyde, AC: acetic acid, PA: propionic acid, AA: acrylic acid.

Table S4 BET data of samples

Sample	S _{BET} (m ² /g)	Vol (cm ³ /g)	Pore size* (nm)
TiPO	43.9	1.7×10 ⁻¹	15.9
KNO ₃ /TiPO	5.3	3.7×10 ⁻²	28.4

*: calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model.

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Sample	200°C (desorption temp.)		350°C (desorption temp.)	
	B acidic sites (mmol/g)	L acidic sites (mmol/g)	B acidic sites (mmol/g)	L acidic sites (mmol/g)
Support	0.01438	0.00666	0.01311	0.00126
Modified catalyst*	0.00000	0.04080	0.00000	0.02690

Figure S1 IR-Py of samples (*: KNO₃ : TPO=4:1, by weight)



Figure S2 Observation of tail gas colour in three sets of experiments using KNO_3/TiPO catalyst ($\text{KNO}_3 : \text{TiPO} = 4:1$)

a: KNO_3/TiPO catalyst with $\text{KNO}_3 : \text{TiPO} = 4:1$, 0.38 mL, 0.30 g; particle size: 20-40 meshes, reaction temp.: 270°C. **No.1**, without LA and pure water, feeding only carrier gas, **No.2**, feeding with pure water as well as carrier gas and **No.3**, feeding LA aqueous solution as well as carrier gas.

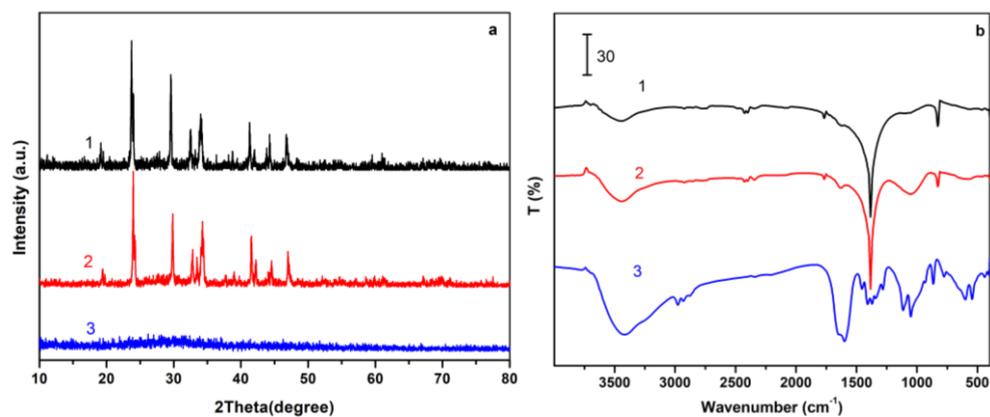


Figure S3 XRD (a) and FT-IR (b) of KNO_3/TiPO catalyst ($\text{KNO}_3 : \text{TiPO} = 4:1$) experienced through three sets of experiments

a: KNO_3/TiPO catalyst with $\text{KNO}_3 : \text{TiPO} = 4:1$, 0.38 mL, 0.30 g; particle size: 20-40 meshes, reaction temp.: 270°C. **No.1**, without LA and pure water, feeding only carrier gas, **No.2**, feeding with pure water as well as carrier gas and **No.3**, feeding LA aqueous solution as well as carrier gas.

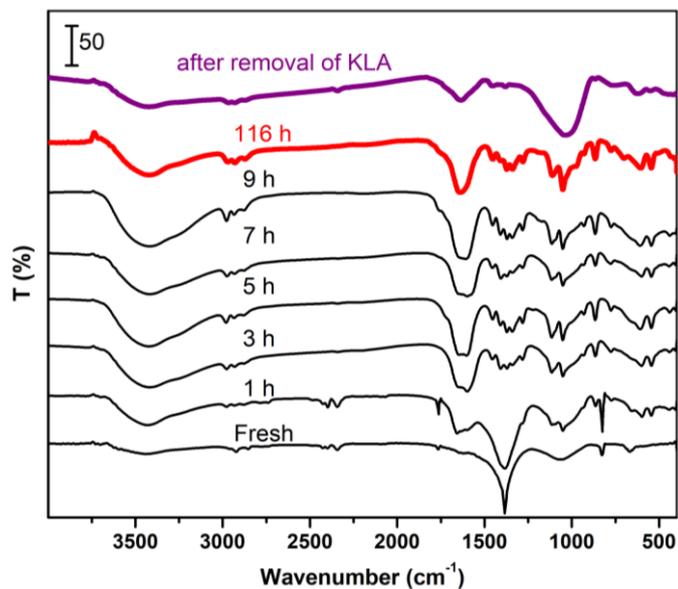


Figure S4 FT-IR spectra of KNO_3/TiPO catalyst ($\text{KNO}_3 : \text{TiPO} = 4:1$) and its corresponding sample by removal of active species

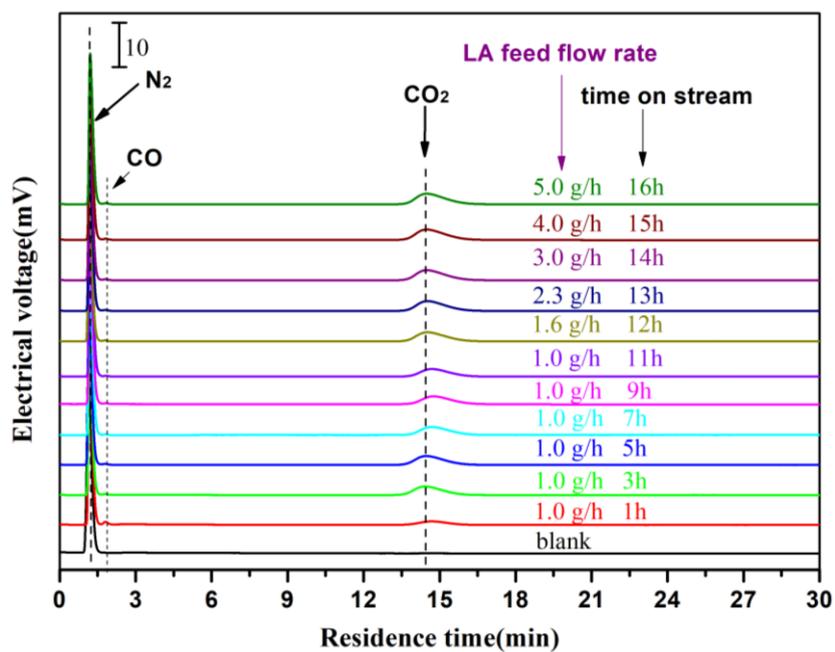
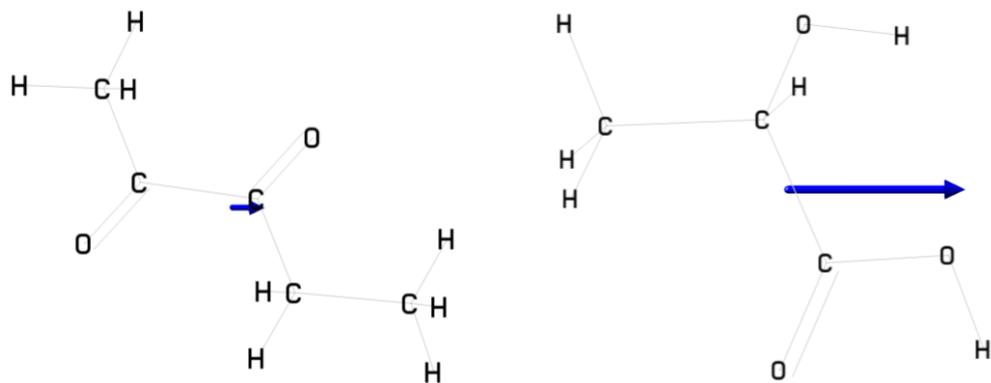


Figure S5 Tail gas analysis with time on stream using GC



dipole moment: 0.1407(Debye)

1.7216(Debye)

molecular volume (V): 136.41044 Angstrom³

107.53266 Angstrom³

Figure S6 Results on dipole moments of 2,3-pentanedione and lactic acid calculated with Gaussian by b3lyp/6-31g(d)

: Based on equation $V=4/3\pi*R^3$, $D=2*R$, we can obtain the diameter (D).

References

1. B. Yan, L. Z. Tao, Y. Liang and B. Q. Xu, *ACS Catal.*, 2014, **4**, 1931-1943.
2. X. L. Li, Y. Zhang, Z. Chen, P. Can, W. X. Zou, C. M. Tang, L. Dong and Y. Wang, *Ind. Eng. Chem. Res.*, 2017, **56**, 14437-14446.