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Supporting Information

Confined alkali metal ion in two-dimensional aluminum phosphate promoted activity for condensation of lactic acid to 2,3-pentanedione

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1 Experimental section

1.1 Catalyst evaluation

The condensation of lactic acid to 2,3-pentanedione was performed with a continuous-flow fixed-bed quartz tubular reactor (4 mm, inner diameter) under atmospheric pressure. 0.19 mL catalyst (20–40 mesh) was placed between two layers of quartz wools inside the reactor. The sample was heated from room temperature to 270°C at a rate of 5°C min^{-1} and kept at that temperature for 1 h by flowing carrier gas of N_2 (1.2 mL min^{-1}) to remove any surface impurities. Then aqueous solution of 20.0 wt.% LA (1.0 mL h^{-1}) was introduced into the reactor, and the reaction was tested for about 10 h. 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).

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

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

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.

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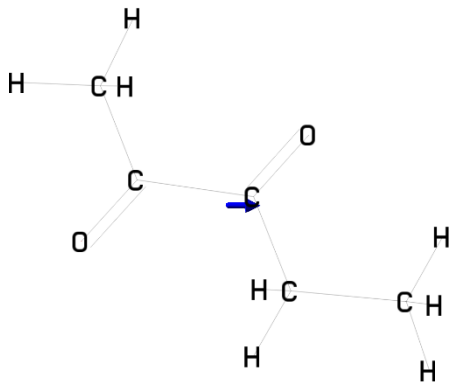
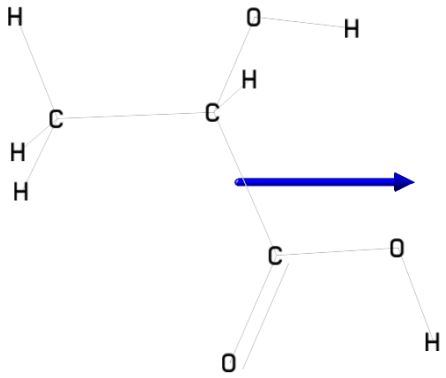
2 Results and discussion

2.1 Molecular diameter and Molecular mean free path



2,3-pentanedione



lactic acid

	2,3-pentanedione	lactic acid
Molecular volume V ($Å^3$)	136.41	107.53
Molecular diameter D (Å)	6.4	5.9
Molecular mean free path S (nm)	41	48

***** Molecular volume V of 2,3-pentanedione and lactic acid is calculated with Gaussian by b3lyp/6-31g(d). Molecular diameter (D) is determined according to equation (a), and molecular mean free path is determined with equation (b).

$V = \frac{4}{3} \times \pi \times (\frac{D}{2})^3$, $D = \sqrt[3]{\frac{6V}{\pi}}$----(a)

$S = \frac{1.38 \times 10^{-23} \times T}{\sqrt{2}\pi \times D^2 \times P} \times 10^9$----(b)

Where S is the molecular mean free path (nm); T is reaction temperature (K), 543K; P is reaction pressure (Pa), atmospheric pressure, 1.013×10^5 Pa; D is molecular diameter (m).

2.2 Diffusion type

(1) Molecular diffusion (bulk diffusion)

$\frac{d}{S} \geq 100$,

(2) Knudsen diffusion

$\frac{d}{S} \leq 0.1$,

(3) Molecular diffusion-Knudsen diffusion coexistence

$0.1 < \frac{d}{S} < 100$,

Where d is the pore diameter (nm) of porous material, and S is molecular mean free path (nm).

2.3 Acidic-basic property

Table S1 CO_2/NH_3-TPD of samples

Catalyst (intercalated alkali metal ion)	Peak area for CO_2-TPD (basic sites) $\times 10^5$	Peak area for NH_3-TPD (acidic sites) $\times 10^4$	Ratio of basicity/acidity
blank	1.68	1.36	12.4
Na^+	2.03	1.98	10.3
K^+	1.65	1.94	8.5
Rb^+	1.22	2.05	5.9
Cs^+	1.26	1.65	7.6

2.4 TG and DTA

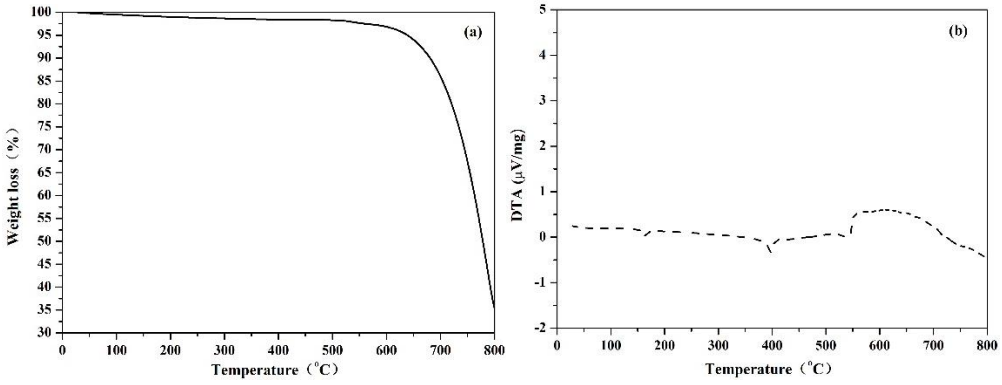


Figure S1 TG profiles of the intercalated Cs^+ /laminar aluminum phosphate after reaction in the presence of only water (without LA) (a) and their corresponding DTA (b)