

Supplementary information

Barium sulphate catalyzed dehydration of lactic acid to acrylic acid

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1 Experimental

1.1 Materials

Lactic acid (analytic grade), was purchased from Chengdu Kelong Chemical Reagent Co. and was used for the dehydration reaction of lactic acid without further purification. Deionized water was prepared in the laboratory and was used to dilute lactic acid for required concentration. Sulphuric acid, barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), acrylic acid, propionic acid, acetic acid, acetaldehyde, 2,3-pentanedione and n-butanol, together with hydroquinone were obtained from Sigma-Aldrich. Acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and acetaldehyde were used for gas chromatograph reference materials, and n-butanol was adopted as internal standard material. Hydroquinone (0.3 wt%) was used as a polymerization inhibitor.

1.2 Preparation of catalysts

BaSO_4 catalyst: Under the condition of continuous stirring at room temperature, 50 mL H_2SO_4 solution with 0.2 mol/L was dropwisely added to 0.09 mol $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 100mL distilled water to form a white precipitate of barium sulphate. Subsequently, the white precipitate was rinsed at least three times to remove dissociative acids such as H_2SO_4 and HCl using distilled water and dried at 120 °C in the air circulating oven for 6 hours. Prior to activity evaluation and characterization, the above catalysts were calcined at desired temperature for 6 hours.

1.3 Catalyst characterization

Powder X-ray diffraction 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 particle size and the morphology of the catalysts were examined using a scanning electron microscope (SEM, JSM-6510). TG analysis was used with Netzsch STA449 F3 analyzer. Surface acidity of the catalyst was tested by Hammett indicator method with standard pretreatment.

1.4 Catalyst evaluation

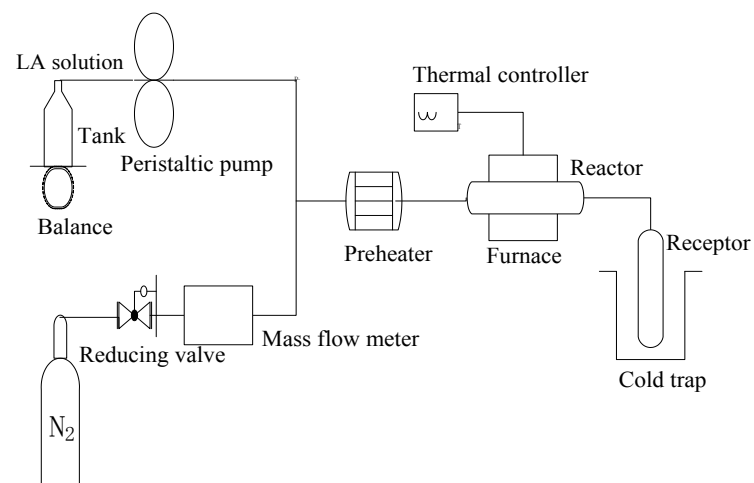


Fig. S1 Experimental set-up for evaluation of the dehydration reaction of lactic acid to acrylic acid

The dehydration of lactic acid to acrylic acid over the catalysts was carried out in a fixed-bed quartz reactor with an 4 mm inner diameter operated at atmospheric pressure and the experimental set-up is shown in Fig.S1. The catalyst (0.50 ~0.60 g, 20–40 meshes) was placed in the middle of the reactor and quartz wool was placed in both ends. Before catalytic evaluation the catalyst was pretreated at the required reaction temperature (400 °C) for 1.0 hour under high purity N₂ (0.1 MPa,

1.0 mL/min). The feedstock (20wt% solution of lactic acid) was then pumped into the preheating zone (lactic acid aqueous solution flow rate, 1.0 mL/h) and driven through the catalyst bed by nitrogen. The contact time of reactant over the catalyst is about 0.5 s, and the contact time is calculated by reference[1]. The liquid products were condensed using ice-water bath and analyzed off-line using a SP-6890 gas chromatograph with a FFAP capillary column connected to a FID. Quantitative analysis of the products was carried out by the internal standard method using *n*-butanol as the internal standard material. GC-MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment. The conversion of lactic acid and the selectivity toward acrylic acid or other by-products were calculated as follows:

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

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

2 Characterization of catalysts

FTIR and XRD

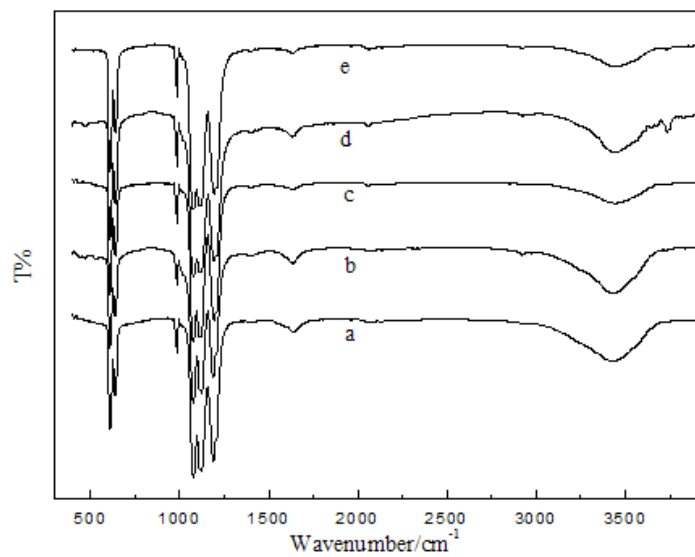


Fig. S2 FTIR spectra of BaSO₄ catalysts at different calcination temperature

a: no calcination, b: 300°C, c: 500°C, d: 700°C, e: 900°C

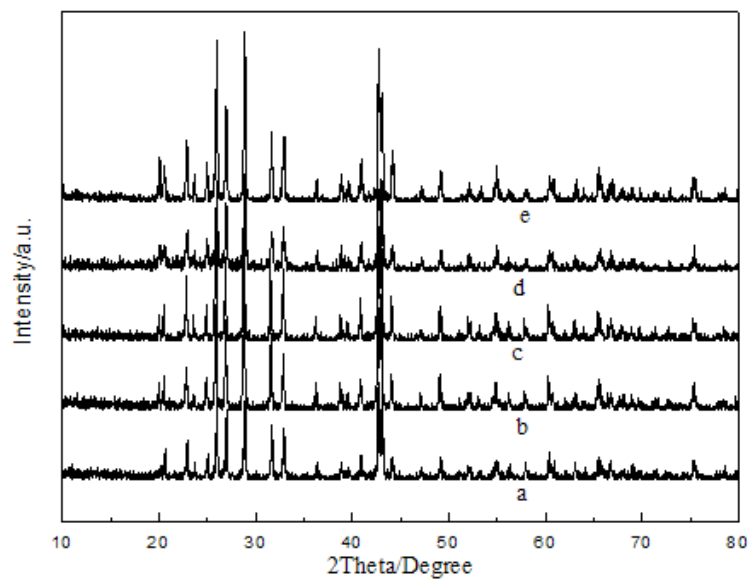


Fig. S3 XRD of BaSO₄ catalysts at different calcination temperature

a: no calcination, b: 300°C, c: 500 °C, d: 700 °C, e: 900°C

SEM and TG analysis

From Fig.S4, morphological appearance of BaSO₄ catalyst almost keep consistent before and after calcination. Less than 1% of mass loss was observed in the range from room temperature to 800°C (shown in Fig.S5).These demonstrated that the BaSO₄ catalyst has an excellent thermal stability.

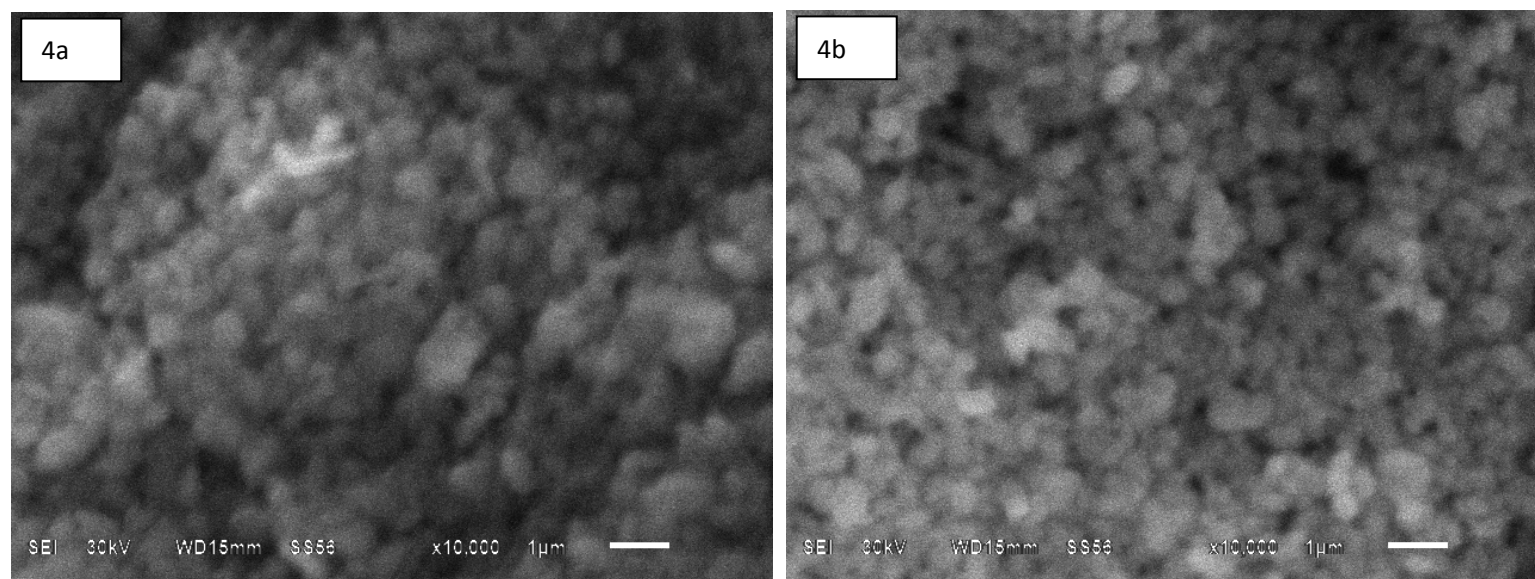


Fig.S4 SEM of BaSO₄ catalyst (4a: calcination temperature at 700°C, 4b: no calcination temperature)

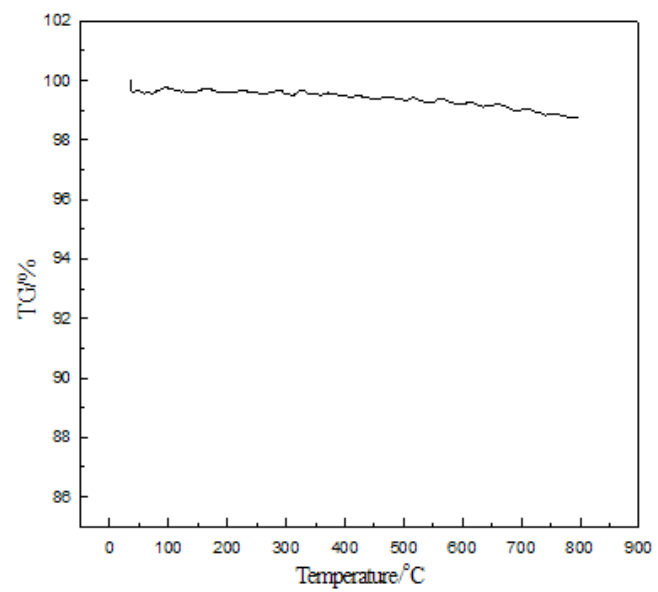


Fig.S5 TG of BaSO₄ catalyst calcined at 500°C

Table S1 BET data of metal sulphates

| Catalyst | BET surface area (m ² /g) |
|---|--------------------------------------|
| Al ₂ (SO ₄) ₃ | 1.77 |
| NiSO ₄ | 15.45 |
| ZnSO ₄ | 1.91 |
| MgSO ₄ | 10.26 |
| BaSO ₄ | 3.36 |
| CaSO ₄ | 5.59 |
| Na ₂ SO ₄ | - |

“-”: BET surface area is very low.

From Table S1, BET surface area of sulphate metals is low. Compared the data of Table 1 with BET data of Table S1, it is clearly seen that the activity of metal sulphates drastically fluctuates with BET surface area. This result indicated that other factor such as surface acidity of metal sulphates is more important than the BET surface area.

3 Evaluation of catalysts

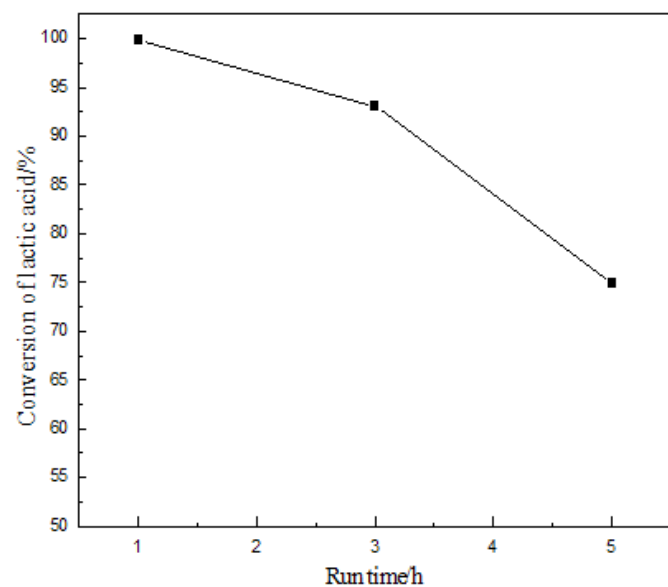


Fig. S6 The performance of CaSO_4 catalyst with time on stream

Conditions: Reaction temperature 400°C , CaSO_4 catalyst 0.5g, carrier gas N_2 1mL/min, feed flow rate 1mL/h, LA feedstock: 20wt% .

From Fig. S6, the conversion of lactic acid drastically decreased with reaction time. When the reaction time is up to 5 hours, the conversion of lactic acid decreased to 74.9%. The selectivity to acrylic acid maintains about 70%.

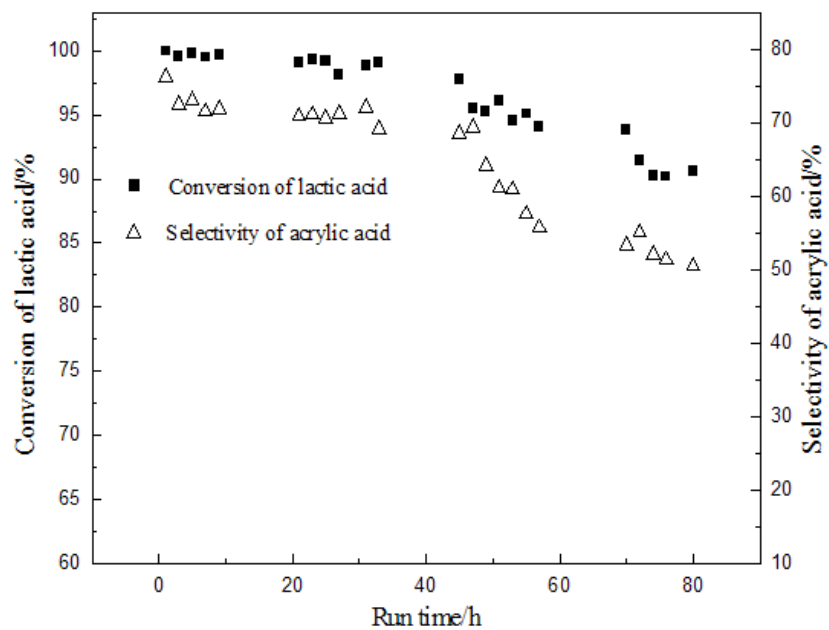


Fig. S7 The performance of BaSO₄ catalyst with time on stream

The stability of BaSO₄ catalyst for dehydration of lactic acid to acrylic acid was shown in Fig. S7. The conversion of lactic acid decreased only 10% when the reaction time is up to 80 hours. Compared this result with that of CaSO₄ catalyst, the former is more stable than the later.

Reference

[1] J.F. Zhang, Y.L. Zhao, M. Pan, X.Z. Feng, W.J. Ji, C.T. Au, *ACS Catalysis* **2011**, *1*, 32.