

Methyl 4-methoxypentanoate: a novel and potential downstream chemical of biomass derived gamma-valerolactone

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Experimental section

GVL, GBL, methanol and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The zeolites including HY, HZSM-5 and USY (Si:Al=14:1) were bought from Nankai University Catalyst Co., Ltd (Tianjing, China).

USY was mixed with NH_4NO_3 with a ratio of 3:8 (w/w) in water and stirred at 80 °C for 8 h followed by distillation, drying and calcining at 550 °C to obtain Hydrogen-exchanged Ultra stable Y-zeolite (HUSY).

$\text{SO}_4^{2-}/\text{USY}$ was prepared by impregnation method. USY was mixed with 10% H_2SO_4 with a ratio of 1:3 (w/v) and standing for 12 h. Then the solid was separated from the mixture, dried at 120 °C for 8 h and calcined at 550 °C for 6 h.

All the solid acid catalysts were stored in a water-free desiccator.

During the experiment, GVL (10 g, 0.1 mol), HUSY (or other zeolites, 0.5g) and CaCO_3 (or other salts, 0.5 mmol) were mixed with 20 mL methanol in a 100 mL Hastelloy batch reactor. The reactor was then sealed and purged with N_2 to 3 MPa at RT. The reactor was then heated to work temperature within 40 min. It should be emphasized that the heating time was not contained in the reaction time recorded. The stirring rate was 700 rpm and kept constantly. After reaction, the heater and stirrer were shut down and the reactor was cooled to RT quickly, and the solid-liquid mixture was filtrated, sealed and stored in the shadow for later analysis. The liquid product prepared in Entry 10 was vacuum distilled at 35 °C to remove methanol, and then heated in an oil bath to separate MMP from GVL and pentenoate esters for detailed characterization.

The qualitative analysis of sample after reaction was conducted with a Thermofisher Trace 1300 & ISQ LT GC-MS instrument with an HB-5 column (15.0 m × 250 μm × 0.25 μm). The following programmed temperature was used in the analysis: 313 K (2 min) – 10 K/min – 653 K (2 min). The carrier gas was He with a flow rate of 1.2 mL/min and the split ratio was 1:50. The mass spectrometer contained an electron impact ionization (EI) with an electron energy of 70 eV and a mass detection range of 40-350.

The amount of GVL and its products were determined on an Agilent 7890 series equipped with a DB-WAXETR capillary column (30.0 m × 250 μm × 0.25 μm) and a flame ionization detector (FID) operating at 543 K. The carrier gas was N_2 with a flow rate of 1.0 mL/min and the split ratio was 1:20. The following programmed temperature was used in the analysis: 313 K (4 min) – 10 K/min – 623 K (4 min). External standard method was applied to measure the content of

GVL, MMP, MP and pentenoates. Typically, GVL conversion and selectivity to MMP, MP and pentenoates were calculated using the following equations:

$$GVL \text{ conversion } (\%) = \left(1 - \frac{n_{GVL}}{n_{GVL_initial}}\right) \times 100\%$$

$$MMP \text{ selectivity } (\%) = \left(\frac{n_{MMP}}{n_{GVL_initial} - n_{GVL}}\right) \times 100\%$$

$$MP \text{ selectivity } (\%) = \left(\frac{n_{MP}}{n_{GVL_initial} - n_{GVL}}\right) \times 100\%$$

$$pentenoate \text{ selectivity } (\%) = \left(\frac{n_{M2P} + n_{M3P} + n_{M4P}}{n_{GVL_initial} - n_{GVL}}\right) \times 100\%$$

It is noted that the amount of M2P and M4P was measured using M3P as internal standard, that is, the response value of M2P, M3P and M4P were treated as equal.

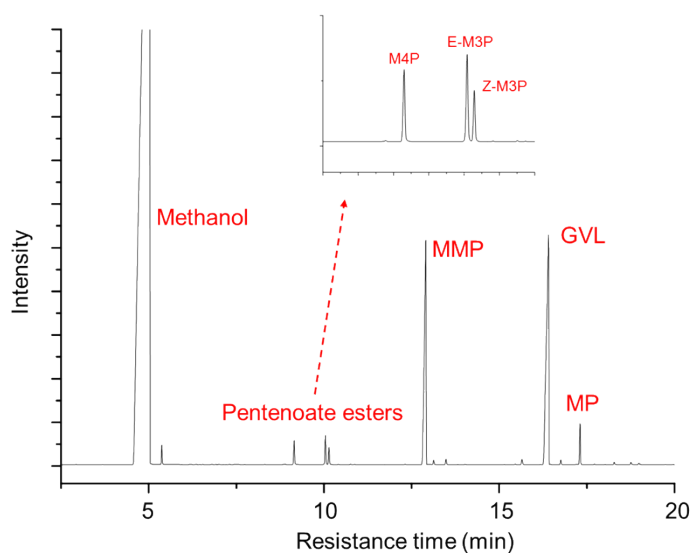


Figure S1 GC spectrum of the product in Entry 4. The main products are pentenoate esters, MMP and MP.

Table S1 The recycle of catalyst

Entry	Treatment	GVL conversion (%)	Selectivity to MMP (%)
S1a	Fresh	46.9	77.8
S1b	1a continuous ^a	32.2	63.2
S1c	1b continuous ^a	23.1	63.3
S1d	Fresh	47.2	78.3
S1e	2a calcine ^b	46.5	77.7
S1f	2b calcine ^b	47.0	78.1

a: The catalyst was applied again with no treatment. b: The used catalyst was calcined at 550 °C for 2 h before reutilization.

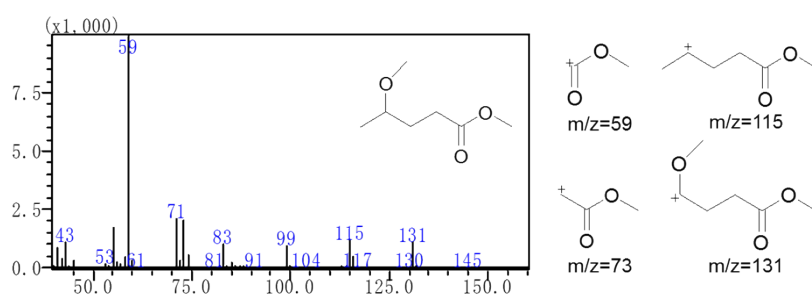


Figure S2 The mass spectrum and supposed fragment ions of MMP

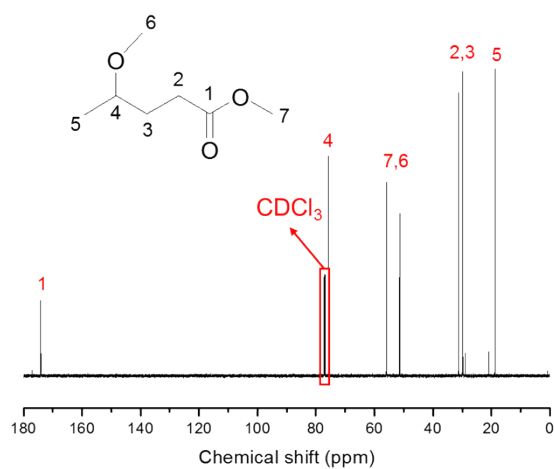
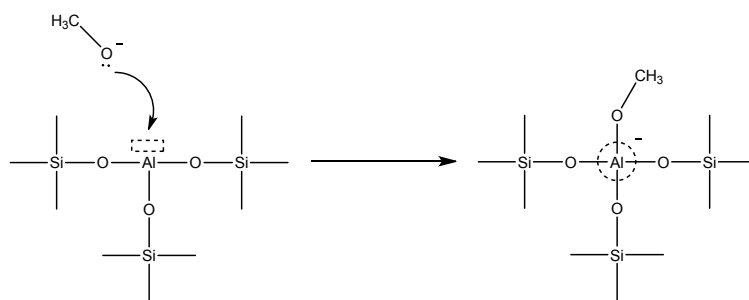


Figure S3 The ^{13}C -NMR spectrum of distilled MMP of Entry 10. The spectra were obtained at a frequency of 150.9 MHz on a Bruker ASCENDTM 600 MHz NMR spectrometer. 93 scans were overlaid to get a higher signal-noise ratio. The small peaks at 20-30 ppm are attributed to residual GVL. $\delta=18.774, 29.937, 31.292, 51.415, 55.982, 75.655, 174.130$.

Table S2 Some physical and chemical properties of GVL, pentenoate esters and MMP

	γ -valerolactone	Methyl Pentenoate	MMP
Appearance	Colorless transparent liquid	Colorless transparent liquid	Colorless transparent liquid
Smell	Fruity	Fruity	Fruity
Density (g/cm³)	1.05	0.89	1.04
Heat value (kJ/g)	25	>25	28
Boiled point (°C)	204	140-150	110 (70 mmHg)
Solubility	Miscible with water	Slightly soluble in water	Insoluble in water



Scheme S1 Proposed inactivity mechanism of the Lewis acidic sites of HUSY by excess CH_3O^- .

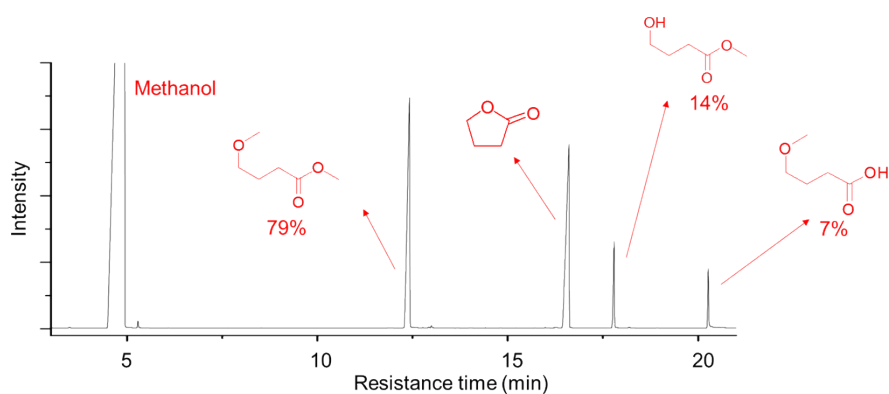


Figure S4 The GC spectrum of GBL ring-opening reaction product, there was no butenoate esters (probable resistance time: 7-10 min) detected

Table S3 Investigation on the effects of CH_3ONa as nucleophile

Entry	Volume of CH_3ONa solution (5 mol/L, μL)	GVL conversion (%)	Selectivity to MMP (%)
S3a	6	53.1	72.7
S3b	18	44.7	65.9
S3c	60	52.2	82.1
S3d	180	9.1	7.7
S3e	600	~0	0

Reaction conditions: 10 mL GVL, 20 mL methanol in total, 0.5 g HUSY, 250 °C, N_2 (with an initial pressure of 3 MPa, RT), 700 rpm, 4 h.