Supporting Information

Reaction Induced Thermal Stabilized TS-1 Zeolite as A Novel Long-Lasting Catalyst for Methyl Lactate Production

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Experimental section

Materials

TS-1 zeolite was purchased from Nankai University Catalyst Co., Ltd (China). Fructose (99%) was bought from Shanghai Macklin Biochemical Co., Ltd (China). Methyl lactate (MLA, 98%), methanol (MeOH, AR), ethanol (ETOH, AR) and ethylene glycol (EG, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Glycolaldehyde dimethyl acetal (GADMA, 98%) was bought from Alfa Aesar (China). Methoxyacetaldehyde dimethyl acetal (MADDA, 98%) was supplied by J & K Scientific (China).

Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were performed on bruker D8 ADVACNCE equipment in a 2θ range of 5-50° with Cu Kα radiation. N_2 adsorption-desorption isotherms were recorded on Micromeritics ASAP 2460 at 77K. All samples had been pretreated for 6 h at 200 °C. Ultraviolet-visible diffuse reflectance spectra (UV−vis) were acquired on Shimadzu UV-3600i Plus in the region of λ = 190-550nm using $BaSO_4$ as background. ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) spectroscopy was performed using a Bruker Avance III 500 spectrometer. Thermogravimetric analysis (TGA) experiments were conducted on Perkin-Elmer Pyris 1 TGA under air flow with a heating rate of 10 °C/min from 50 to 850 °C. Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iS50. Temperature-programmed desorption mass spectrometry (TPD-MS) ware carried out using Micromeritics AutoChem II 2920 chemisorption analyzer, equipped with a thermal conductivity detector (TCD) and coupled to an online mass spectrometer (MS, HIDEN QIC-20). About 0.1 g of catalyst was treated at 200 ℃ for 2 h under Helium atmosphere to remove impurities and then cooled to 50 ℃. Afterward, the temperature was raised to 800 °C to obtain the TCD signal, and the related species signal is detected by an online mass spectrometer.

Catalytic reactions

The catalytic reactions were carried out in a 14 mL stainless steel autoclave reactor. Before the reaction, a certain amount of fructose was dissolved in methanol to obtain the solution with fructose concentration of 10 g/L. In a typical run, a certain amount of catalyst and 6 mL the above solution were added into the reactor. Next, the sealed reactor was placed into preheated furnace at desired temperature. At the end of the reaction time, the autoclave was rapidly transferred in cool water to stop the reaction. The reaction solution was diluted with methanol and then filtered with a 0.22 μm organic filter membrane for further analysis.

For the recycling tests, the spent catalysts were separated from the reaction by centrifugation, washed with methanol thoroughly, dried under 70 °C and then used in the next run.

The pretreatment process of TS-1 zeolite was as follows: a certain amount of TS-1 zeolite and solvent (20 mL/g TS-1) were added into a Teflon-lined autoclave. Subsequently, the reactor was placed into an oil bath which was previously heated to 180 °C and kept for different reaction time with stirring. Afterwards, the catalyst was separated by centrifugation, washed with deionized water and dried at 70 °C to obtain pretreated-TS-1 zeolite.

Product analysis

Fructose was quantitatively analyzed using high performance liquid chromatography (HPLC, Agilent 1100) with an Aminex HPX-87H column (300 mm×7.8 mm) and refractive index detector (RID) with 5 mmol/L H_2SO_4 as mobile phase (0.4 mL/min) and the column temperature of 60 °C. MLA, GADMA and MADDA were analyzed via gas chromatography (GC, Agilent 7890A) equipped with a HP-5 column (30 m×0.32 mm×0.25 μm) and a flame ionization detector (FID). The conversion of fructose and yield of products were calculated by the following equations:

$$\text{Fructose conversion}\ (\%) = 1 - \frac{\text{Moles of fructose remaining in the reaction}}{\text{Moles of initial fructose}} \times 100\%$$

$$\text{MLA yield (\%)} = \frac{\text{Moles of MLA}}{(\text{ Moles of initial fructose }) \times 2} \times 100\%$$

$$\text{GADMA (or MADDA) yield (\%)} = \frac{\text{Moles of GADMA (or MADDA)}}{(\text{ Moles of initial fructose}) \times 3} \times 100\%$$

The experimental result was the average of the three parallel experiments, and the error was the standard deviation of the results of the three samples.

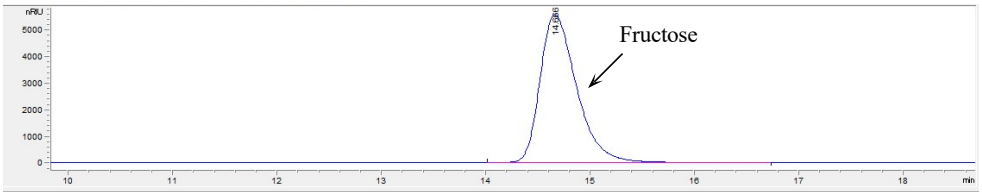

Figure S1. Liquid chromatogram of fructose.

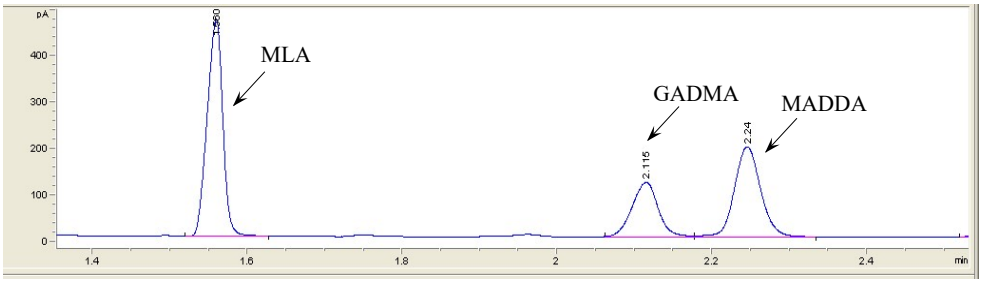

Figure S2. Gas chromatograms of methyl lactate (MLA), glycolaldehyde dimethyl acetal (GADMA) and methoxyacetaldehyde dimethyl acetal (MADDA).

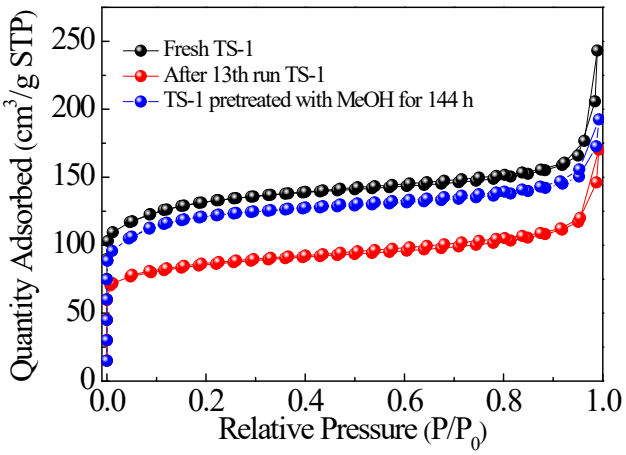

Figure S3. N_2 adsorption−desorption isotherm of fresh, reused and pretreated TS-1 zeolites.

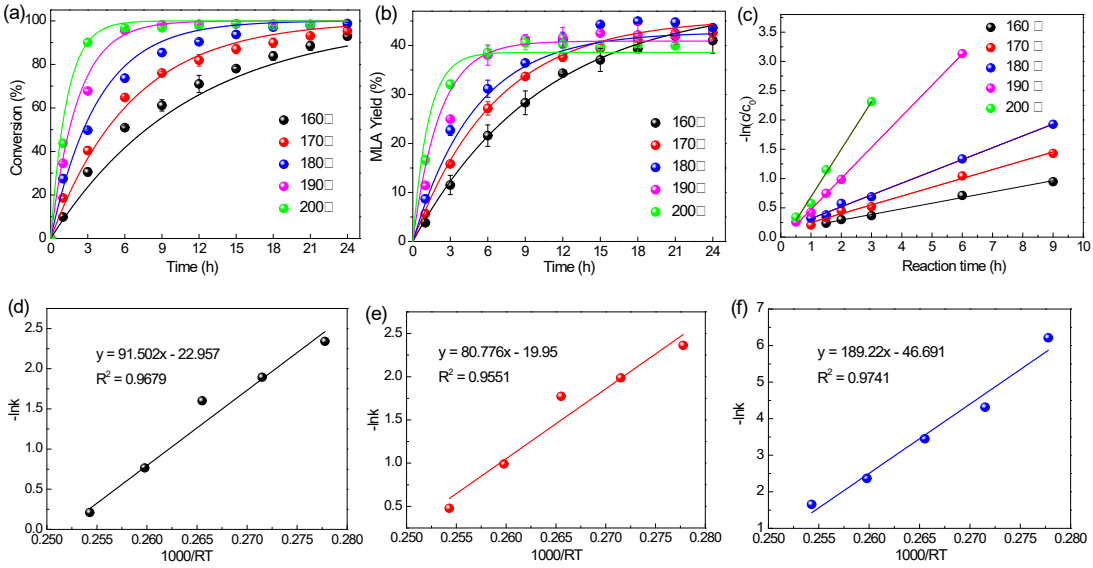

Figure S4. (a, b) Kinetic studies of fructose conversion over pretreated-TS-1. Reaction conditions: catalyst (0.03 g), fructose (0.06 g), methanol (6 mL). (c) The first-order plot of $\ln(c/c_0)$ versus reaction time. Arrhenius plot of -lnk versus 1/T of (d) fructose conversion (black line), (e) MLA yield (red line) and (f) other by-products (blue line) over pretreated-TS-1 at different temperatures.

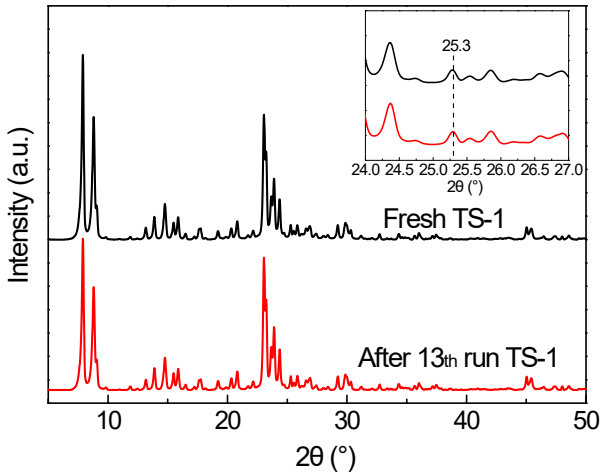

Figure S5. XRD patterns of fresh and reused TS-1 zeolites.

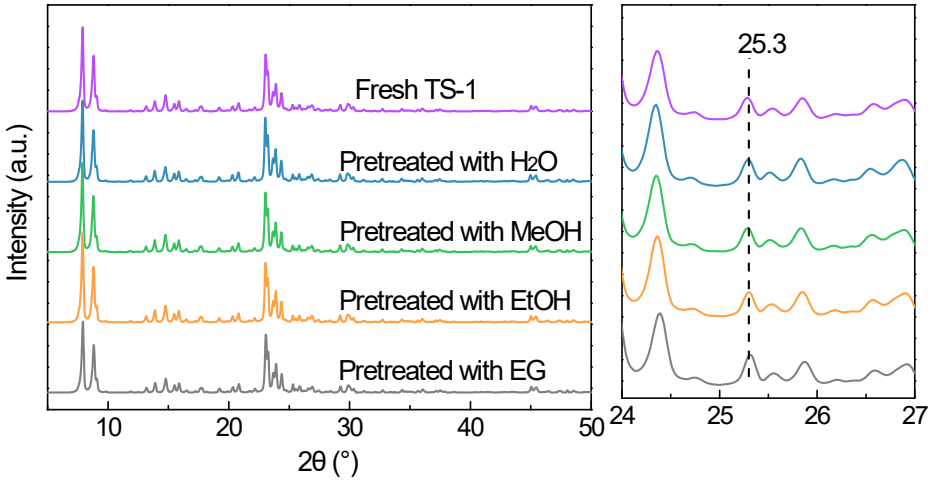

Figure S6. XRD patterns of TS-1 zeolites pretreated with different solvents under 180 °C for 144 h.

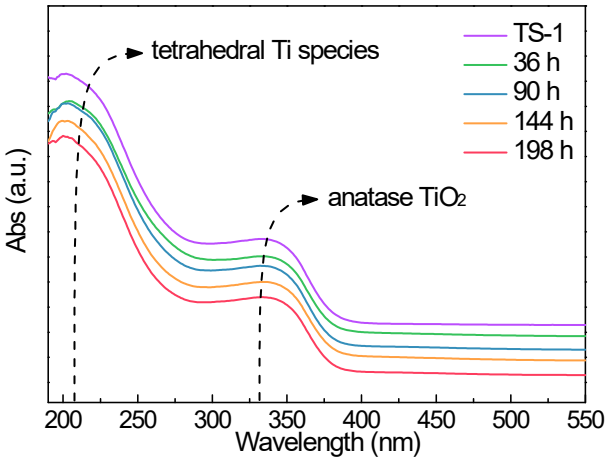

Figure S7. UV-vis spectra of TS-1 zeolites. 36 h, 90 h, 144 h and 198 h represent TS-1 zeolite pretreated with MeOH for 36, 90, 144 and 198 h, respectively.

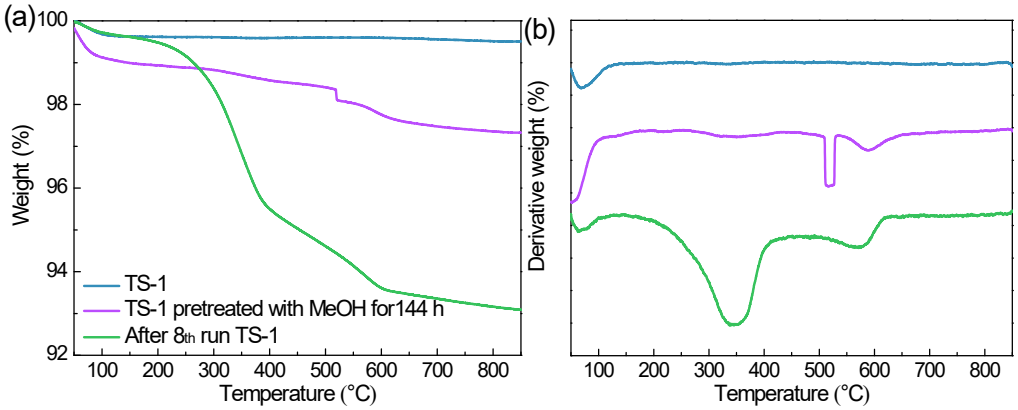

Figure S8. (a) TGA and (b) DTG curves of TS-1 zeolites.

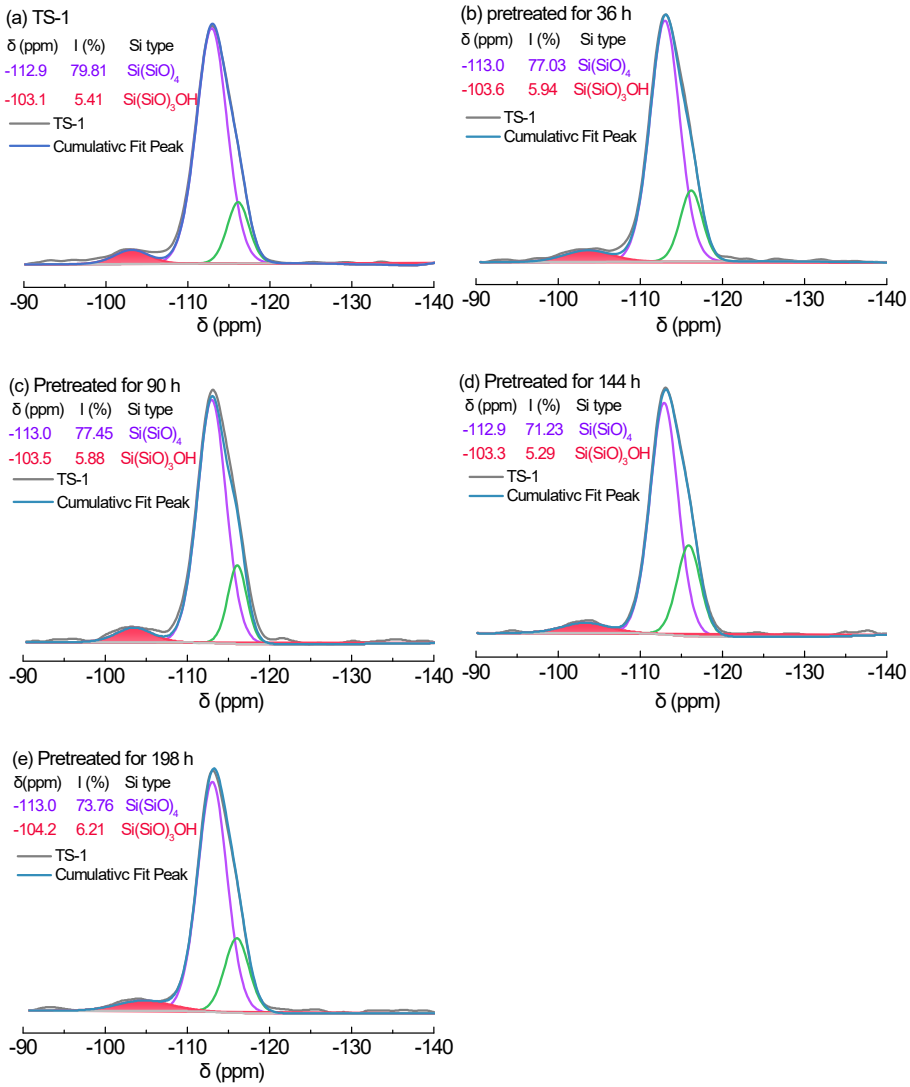

Figure S9. ^{29}Si MAS NMR spectra of (a) fresh TS-1 and TS-1 pretreated with methanol for (b) 36 h, (c) 90 h, (d) 144 h and (e) 198 h.

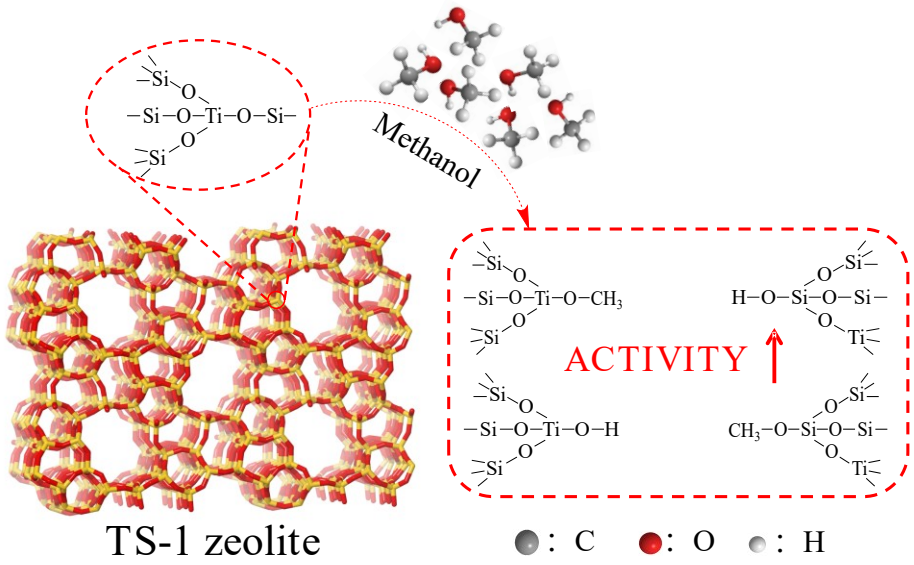

Figure S10. Possible activation mechanism of methanol pretreatment on TS-1 zeolite.

Table S1. Comparison of the stability of catalysts modified by aluminosilicate zeolites.

Catalysts	Substrate	Number of cycles	MLA yield loss relative to the first run	Regeneration process	Ref.
Sn-Beta-H4	glucose	5	19.7%	Calcination in air after 4th run to recover activity	1
Sn-Beta			46.7%		
Nb/HUSY	fructose	4	about 9%	Calcination at 700 °C before next run	2
Sn-Beta and H-Beta	levoglucosan	5	about 28.6%	Calcination at 550 °C before next run	3
Sn-Beta	glucose	5	about 13%	Calcination at 550 °C before next run	4
Sn-SCM-1	glucose	4	18.4%	Calcination in air after 3rd run to recover activity	5
Sn-MCM-22			57%		
Sn–Al-USY	glucose	4	about 47.6%	Calcination in air after 3rd run to recover activity	6
Au/Sn-USY	glycerol	3	16.5%	Not mentioned	7
TS-1	fructose	14	Without deactivation	Without calcination	This work

Table S2. Textural properties of TS-1 zeolites.

	S_{BET}[a]	S_{Micro}[b]	V_{Total}[c]	V_{Micro}[b]

	(m^2/g)	(m^2/g)	(cm^3/g)	(cm^3/g)
Fresh TS-1	488.33	393.39	0.38	0.16
After 13th run TS-1	315.48	237.01	0.26	0.10
TS-1 pretreated with MeOH for 144 h	447.63	376.14	0.30	0.15

[a] Calculated by the Brunauer-Emmett-Teller (BET) equation.

[b] Acquired by t-plot method.

[c] Evaluated at P/P_0 of approximately 0.99.

Table S3. Reaction rate constants (k) of fructose transformation at different temperatures.

T/K	k/h^{-1}	R^2
433	0.0962	0.9939
443	0.1505	0.9926
453	0.2017	0.9972
463	0.4654	0.9831
473	0.8110	0.9916

Table S4. Reaction rate constants of MLA (k_1) and by-products (k_2) formation at different temperatures.

T/K	k_1/h^{-1}	k_2/h^{-1}
433	0.0942	0.0020
443	0.1371	0.0134
453	0.1699	0.0318
463	0.3713	0.0941
473	0.6197	0.1913

Table S5. the ratio of Q^4/Q^3 of TS-1 zeolites

Blank TS-1	Methanol-pretreated TS-1

		36 h	90 h	144 h	198 h
Q^4/Q^3	15	13	13	13	12

References

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