Supporting Information

An encapsulation strategy to design In-TS-1 zeolite enabling high activity and stability toward efficient production of methyl lactate from fructose

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Experimental section

Materials

Methyl lactate (98%), methanol (AR), isopropanol (IPA, AR), and tetrapropylammonium hydroxide (TPAOH, 25wt% aqueous solution) were supplied by Sinopharm Chemical Reagent Co., Ltd (China). Fructose (99%), titanium butoxide (TBOT, 99%), indium chloride ($InCl_3$, 99.9%), and tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd (China). Tetraethyl orthosilicate (TEOS, 99%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99.99%), iron chloride ($FeCl_3$, 99.9%), and Indium oxide (In_2O_3) were provided by Aladdin Chemical Reagent Co., Ltd (China). Nickel(II) chloride Anhydrous ($NiCl_2$, 98%) was purchased from Tokyo Chemical Industry Co., Ltd (Japan). Glycolaldehyde dimethyl acetal (GADMA, 98%) was obtained from Alfa Aesar (China). Methoxyacetaldehyde dimethyl acetal (MADDA, 98%) was bought from J & K Scientific (China).

Catalyst preparation

In-TS-1 zeolite was synthesized via hydrothermal method. In a typical run, a certain amount of $InCl_3$ was dissolved in 14.8 mL of deionized water and stirred for 10 min. Then, 15.63 g TEOS and 6.72 g TPAOH were introduced into the above solution and stirred for 5 h, the mixture was recorded as solution A. Next, 0.6381 g TBOT, 6.1 g IPA, 5.48 g TPAOH, and 12.2 mL deionized water were sequentially added into a new flask and hydrolyzed for 2 h, which was denoted as solution B. Afterwards, solution B was added dropwise into solution A under stirring. After thorough stirring for 2 h, the resulting gel with the molar composition of 1 TEOS:0.025 TBOT:(0.0025-0.03) $InCl_3$:0.2 TPAOH:20 H_2O was obtained. The final gel was transferred into a 100 mL Teflon-lined stainless steel autoclave and crystallized at 170 ℃ for 3 days. The solid sample was thoroughly washed with deionized water, dried at 70 ℃, and calcined at 550 ℃ for 6 h. The as-synthesized zeolites were designated as In-TS-1-x where x represented the molar ratio of

n($InCl_3$):n(TEOS) or n(In):n(Si). Replacing $InCl_3$ with $CoCl_2 \cdot 6H_2O$, $FeCl_3$, $NiCl_2$ and $SnCl_4 \cdot 5H_2O$ to obtain Co-TS-1, Fe-TS-1, Ni-TS-1, Sn-TS-1, respectively, and the ratio of n(metal):n(Si) was 0.01. TS-1 zeolite was synthesized as above, except that no metal chloride salt was added.

Product analysis

Quantification of fructose by 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 was 60 ℃. Quantitative analysis of MLA, GADMA and MADDA by 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:

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

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

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

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.

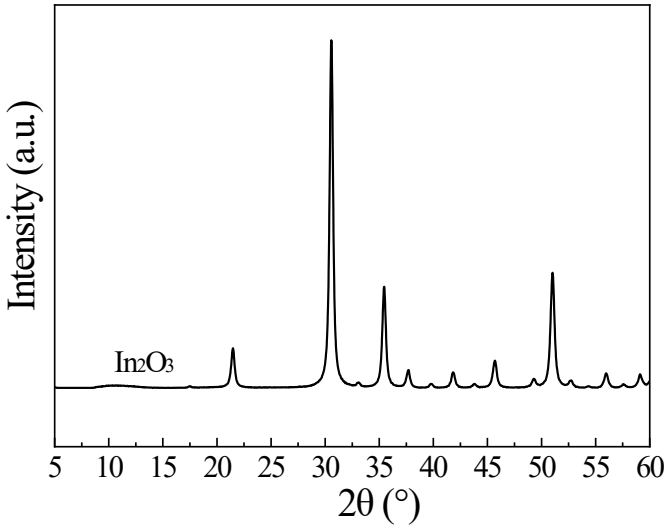

Fig. S1. XRD patterns of In_2O_3.

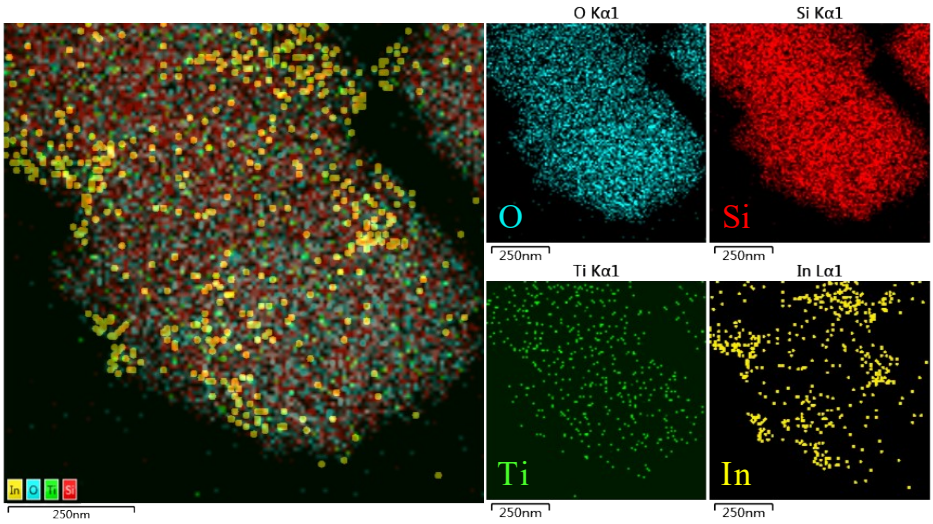

Fig. S2. Element mapping analysis of In-TS-1-0.03.

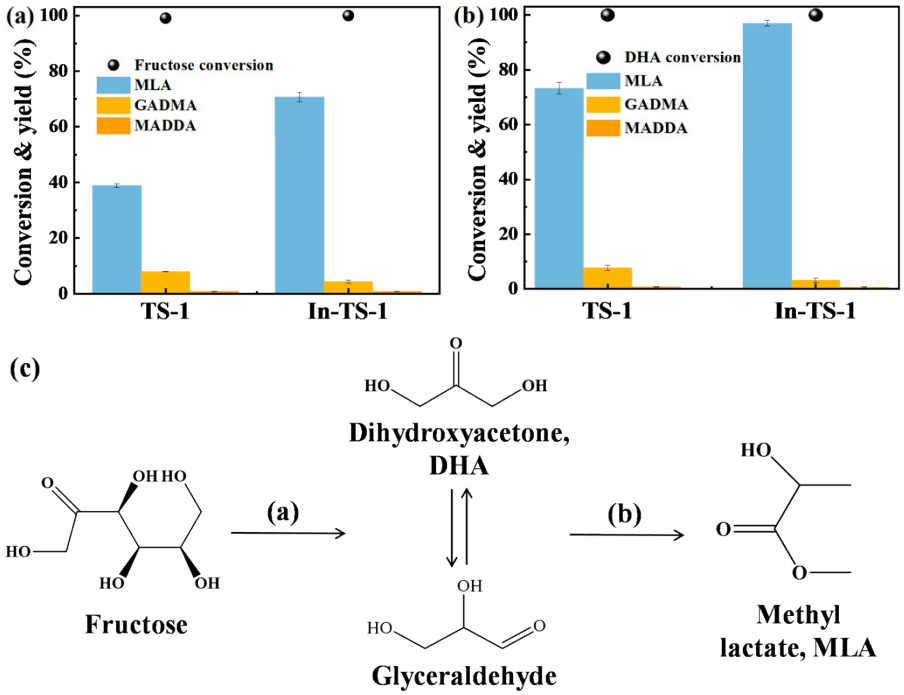

Fig. S3. Conversion of (a) fructose and (b) DHA to MLA over TS-1 and In-TS-1. Reaction conditions: 60 mg of fructose, 30 mg of catalyst, 6 mL of methanol, 180 °C, 15 h. (c) Reaction pathway of fructose to MLA.

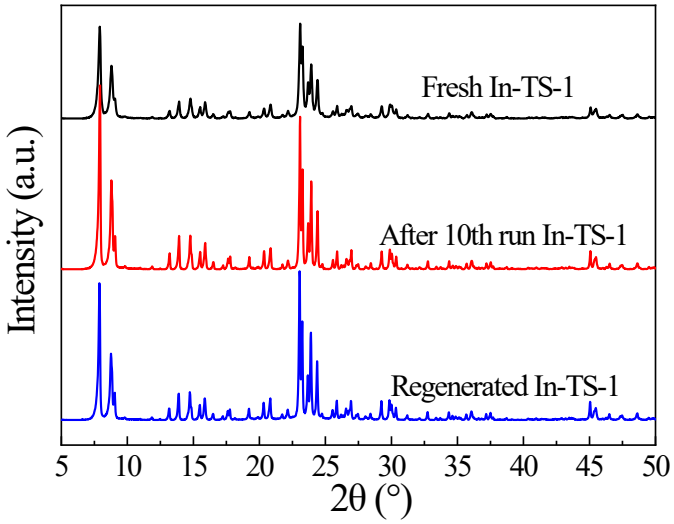

Fig. S4. XRD patterns of fresh, reused, and regenerated In-TS-1-0.02 zeolites.

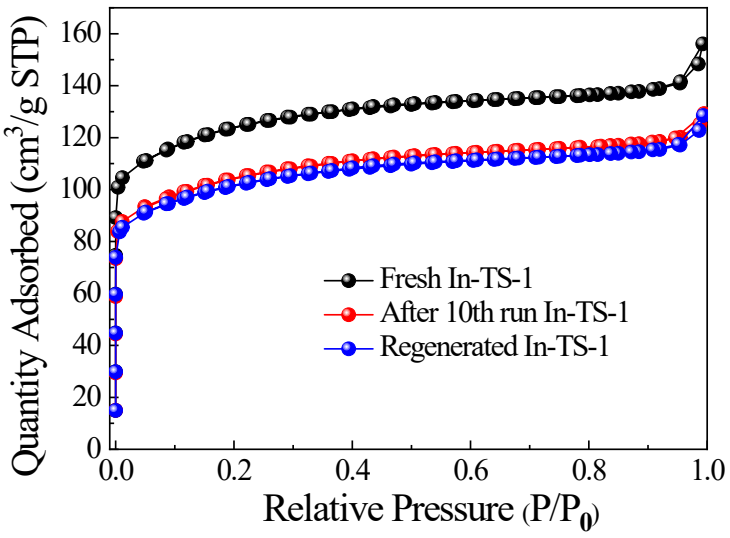

Fig. S5. N_2 adsorption−desorption isotherm of fresh, reused, and regenerated In-TS-1-0.02 zeolites.

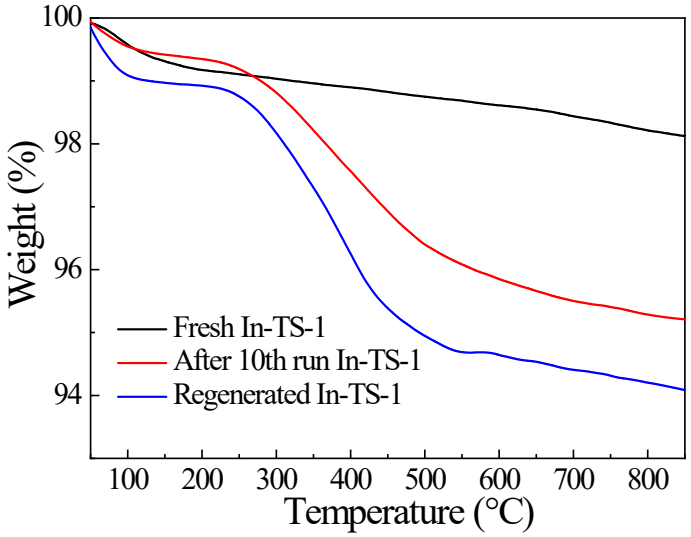

Fig. S6. TGA curves of fresh, reused, and regenerated In-TS-1-0.02 zeolites.

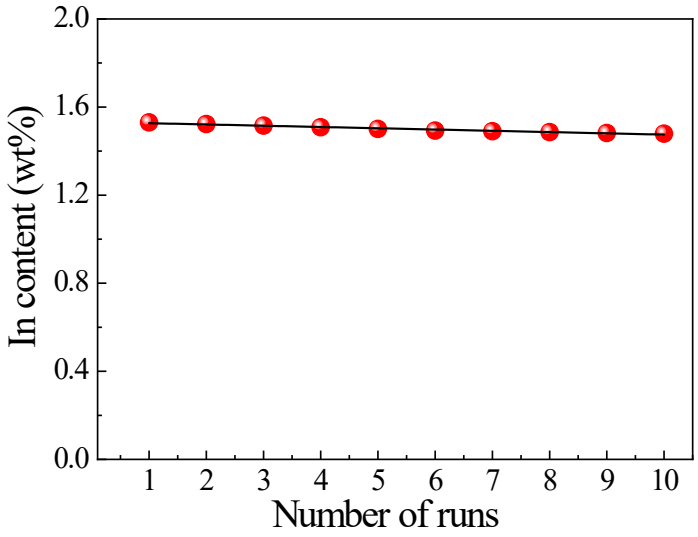

Fig. S7. ICP-OES data for the In content of In-TS-1-0.02 per cycle.

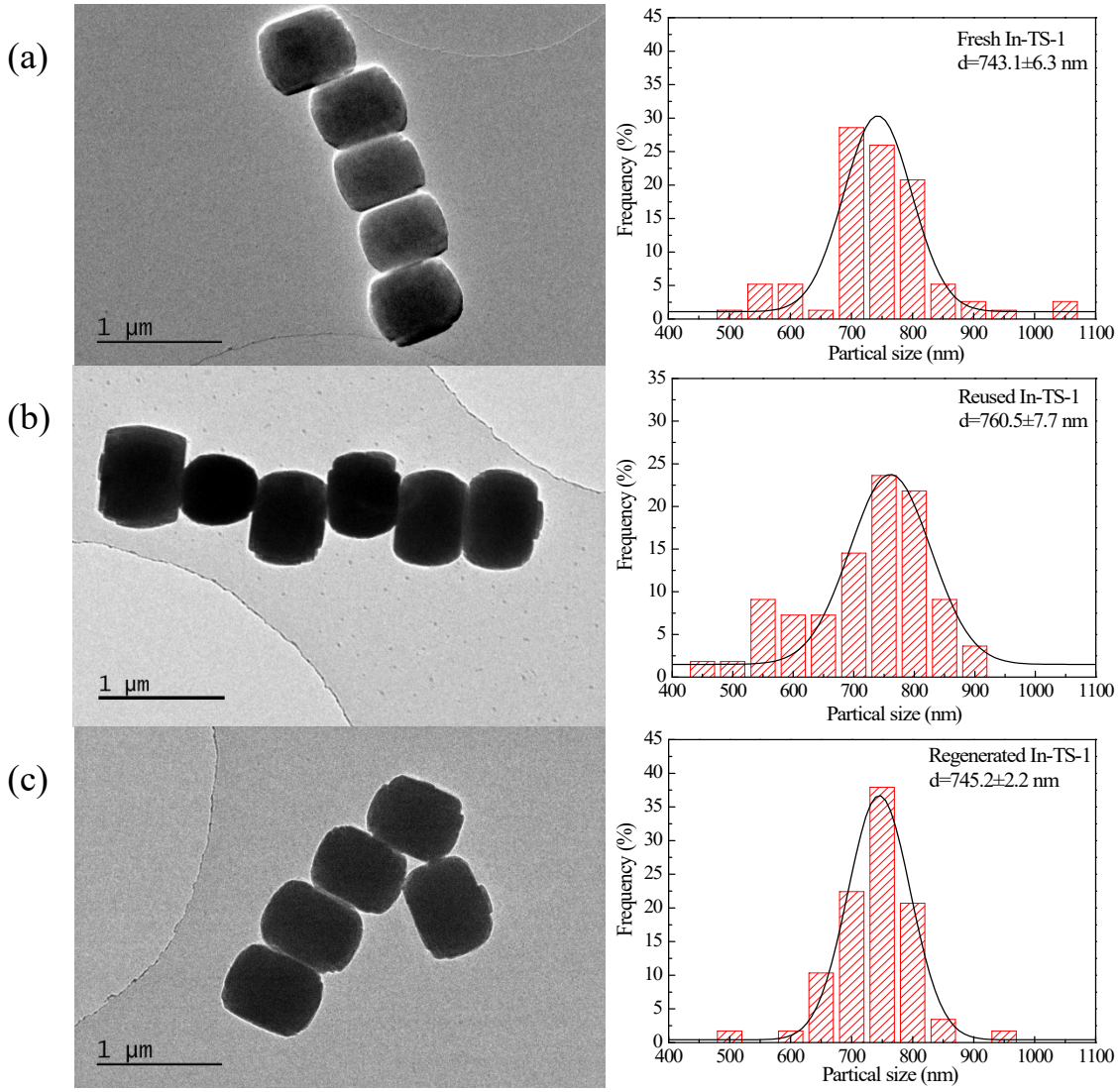

Fig. S8. Particle size distribution histograms of (a) fresh, (b) reused, and (c) regenerated In-TS-1-0.02 zeolites. The average mean particle sizes were estimated by counting the diameter of more than 50 random particles from multiple TEM images.

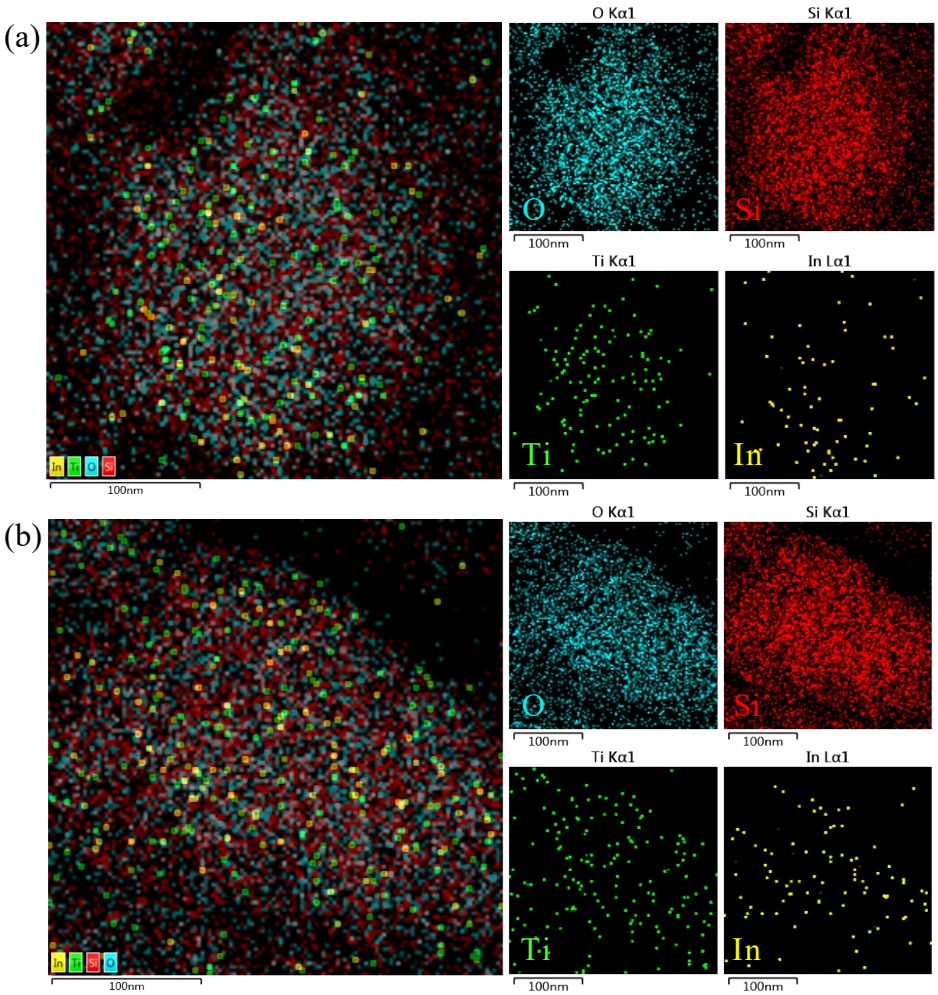

Fig. S9. Element mapping analysis of used In-TS-1-0.02 (a) before and (b) after regeneration. Before the measurements, samples were cut into thin slices and dropped onto a Mo grid coated with a carbon membrane.

Table S1 Relative crystallinity of In-TS-1 zeolites with different In/Si molar ratios.

In/Si molar ratio	Relative crystallinity (%)[a]
TS-1	100
0.0025	93.4
0.005	87.4
0.01	86.3
0.015	85.0
0.02	86.3
0.025	82.0
0.03	46.9

[a] The relative crystallinity of In-TS-1 is determined relative to TS-1 zeolite

Table S2 Acidic properties calculated from pyridine-FTIR

Catalysts	Acid amounts (μmol·g^{-1})		
	Brønsted acid	Lewis acid	Total acid
TS-1	20.8	400.9	421.7
Co-TS-1	22.9	408.8	431.7
Fe-TS-1	136.4	218.0	354.4
In-TS-1	28.4	424.9	453.3
Sn-TS-1	45.5	442.6	488.1
Ni-TS-1	17.2	371.3	388.5

Table S3 Leaching of active sites determined by ICP-OES.

Catalysts	Element	Leaching (wt.%)							
		1	2	3	4	5	6	7	Total
Sn-TS-1-0.01	Sn	0.61	1.57	1.49	1.75	1.44	0.99	0.81	8.66
In-TS-1-0.01	In	0.38	0.29	0.3	0.27	0.46	0.55	0.58	2.83

Table S4 Content of indium in In-TS-1 catalysts.

In/Si molar ratio[a]	Actual In content (wt%)[b]
0.01	1.02
0.02	1.53
0.03	2.03

[a] Molar ratio of In/Si in the catalyst preparation process.

[b] Determined by ICP-OES.

Table S5 Comparison of pseudo-yield of retro-aldol reaction.

Catalysts	MLA yield (%)		Pseudo-yield of retro-aldol reaction (%)[a]
	from fructose	from DHA	
TS-1	38.8	73.3	52.9
In-TS-1-0.02	70.7	97.0	72.9

[a] *pseudo-yield of retro-aldol reaction = (MLA yield from fructose)/(MLA yield from DHA)*

Table S6 Reaction rate constants (k) of fructose transformation at different temperatures.

T/K	k/h^{-1}	R^2
433	0.2952	0.9639
443	0.352	0.9774
453	0.5238	0.9916
463	0.8324	0.9926
473	1.2937	0.9967

Table S7 Comparison of activity and stability of different catalysts

Catalysts	Substrate	MLA yield (Reaction conditions)	Number of cycles[a]	MLA yield loss	Regeneration process	Ref.
Sn-Beta	Sucrose	68% (160°C, 20 h)	6	Without deactivation	Calcination at 480 °C before the next run	1
Sr-Sn-Al-Beta	Glucose	53% (180 °C, 24 h)	3	37%	Calcination at 400 °C before next run, but unable to regenerate	2
Sn-In-MCM-41	Glucose	69.4% (160°C, 20 h)	4	13%	Without calcination	3
Sn-Ni-Beta-WQ	Starch	--	8	about 11%	Calcination at 550 °C after 4th run to recover activity	4
Sn-Ni-Beta-DF		--	8	about 11%		
Fe-Sn/Beta	Glucose	67% (220 °C, 6 h)	5	6.1%	Calcination at 550 °C before the next run	5
Sn-SCM-1	Glucose	55.3% (170 °C, 20 h)	4	about 10%	Calcination in air after 3rd run to recover activity	6
Sn-MCM-22		46.2% (170 °C, 20 h)		about 24%		
Sn–Al-USY	Glucose	43.2% (170 °C, 6 h)	4	about 20%	Calcination at 550 °C after 3rd run to recover activity	7
In-TS-1-0.01	Fructose	65.9% (180 °C, 15 h)	7	4.4%	Without calcination	**this work**
Sn-TS-1-0.01		56.7% (180 °C, 15 h)		10%		
In-TS-1-0.02		43.4% (170 °C, 3 h)	14	5.0%	Methanol pretreatment before the 11th run	

[a]Conversion of sugar was approximately 100% except In-TS-1-0.02 (71.2% conversion)

Table S8 Textural properties of In-TS-1-0.02 zeolites.

Catalysts	S_{BET}[a] (m^2/g)	S_{Micro}[b] (m^2/g)	V_{Total}[c] (cm^3/g)	V_{Micro}[a] (cm^3/g)
Fresh In-TS-1	459.2	277.1	0.24	0.11
After 10th run In-TS-1	383.4	228.0	0.20	0.09
Regenerated In-TS-1	373.2	233.7	0.20	0.10

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

[b] Obtained by t-plot method.

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

References

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