Electronic Supplementary Material (ESI) for Green Chemistry.

Water-Induced Efficient Isomerization of Glucose into Fructose over the Lithium Loaded Silicalite-1 Catalyst at 50 °C

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General Information

All chemicals were used as received from the commercial suppliers:, mannose (≥99%), fructose (≥99 %), LiCl (AR, ≥99.0 %), glucose (AR, 99.0 %),lactic acid(AR, ≥99%), formic acid (AR, ≥99 %),. All reactions were performed in a 100.0 mL Parr pressure reactor. Centrifugation of the reaction mixture was performed on Thermo LYNX6000 (3000 rpm, 10 min).

Carbon-13 Nuclear Magnetic Resonance Spectrometry (^{13}C NMR): Agilent 500 MHz (125MHz), The product was dissolved in D_2O and scanned 1024 times.

X-Ray powder diffraction (XRD) patterns of the catalysts were performed on Rigaku Ultima IVX-Ray diffractometer using Cu Kα radiation in the 2θ range from 5 ° to 80 ° at a scan rate of 2°/min.

Scanning electron microscope (SEM) analysis: The Supra 55 Sapphire field emission scanning electron microscope of Carl Zeiss (shanghai) Co was used to analyze the morphology of the catalyst. The test voltage was 15 KV, catalyst powder needed to be taken for gold spraying before the test.

Pyridine adsorption Fourier-transform infrared (Py-IR): The catalyst was detected by the FT-IR Nicolet 670. Weigh out 0.05 g of catalyst, press it into a translucent sheet in a tablet press, and place it in the sample tank (the material of the sample tank and the window is quartz). The sample tank was evacuated and treated at 200 °C for 2 h, after which the temperature was lowered to room temperature and the sample background spectrum was measured. Firstly, the pyridine gas is introduced into the sample tank to absorb the saturation of the sample. Raise the sample temperature to 200 °C and hold it for 1 h to measure the spectrum at 200 °C. After that, the temperature was increased to 350 °C for 1 h, and infrared spectra of pyridine adsorption at 200 °C and 350 °C were obtained.

Analysis of specific surface area of nitrogen adsorption (BET): Micromeritics, TriStar Ⅱ3020, The sample to be tested is first degassed at 300 °C for more than 3 h, and then tested with N_2 as the medium at -196 °C.

Inductively coupled plasma-atomic emission spectrometry (ICP): Perkin Elmer Optima 8000, digest and filter a certain amount of catalyst to measure the content of Li.

UV Vis absorption spectrum: Agilent Spectrophotometer technologies Cary 5000 UV vis-NIR, measuring wavelength range: 200-500 nm.

Total Organic Carbon (TOC): Shimadzu TOC-LCSH/CPH, Liquid products need to be diluted, range : 4 μg/L~30000 mg/L. According to the TOC results, the carbon balance was >99.9 % when Li-S1 as the catalyst in 50 °C.

The data were recorded on the HPLC (Shimadzu LC-20A, Aminex HPX-87H Ion Exclusion Column: 300 mm × 7.8 mm. RID-10A). Analysis condition: column temperature 50 °C, injection volume 10 μL, the mobile phase 12.5 mmol/L H_2SO_4, 0.60 ml/min. After reaction, the solids were separated by filtration and the composition of the liquid phase was analyzed by HPLC. Besides the main product fructose and glucose, a variety of other compounds were detected in more than 80 °C, which were comprehensively analyzed. By drawing a standard working curve with the standard product of the specific component to be tested, and then measuring the content of the component in the sample under the exact same chromatographic conditions, the concentration can be found from the working curve. Conversion and yield values were calculated based on the equations shown in the quantification part.

Recycling Test

After a typical catalytic run (300 mg Li/S-1 catalyst, 30 ml water,50 °C, 1 h, 1 MPa N_2), the catalyst was separated from the reaction solution by centrifugation and subsequent decantation. The solid was additionally washed with water (5*30 ml) and dried overnight at room temperature under vacuum prior to the next run.

Preparation of Li/S-1 catalyst

S-1 zeolite preparing: Accurately weigh 23.5 g TEOS, 36.7 g TPAOH (25 %) and 33.9 g H_2O mix well. Stir while reacting at room temperature for 6 h. After the reaction, transfer it to the crystallizing kettle, and put it into the oven at 170 °C for 3 days. After taking it out, it was washed and centrifuged, dried and baked at 550 °C for 3 h.
Li/S-1 catalyst preparing: Take 2.0 g S-1 zeolite and 0.12 g LiCl into bowl and carefully grand for 30 min, then put the mixture into muffle furnace and baked at 550 °C for 3 h.

Quantification

The yield of products was calculated based on the number of carbons in the product as follows: where represents the number of carbons and C_i is the molar concentration of the compound i, $C_{glucose}$ indicates molar concentration of glucose before the reaction.

$$\text{Yield } /\% = (C_i / C_{glucose}) \times 100\ \%$$

Conversion was based on the molar carbon concentration of the compounds according to the equations below, where $C_{glucose}$ indicates the molar carbon concentration of glucose before the reaction and $C_{glucose}$' indicates the molar carbon concentration of glucose after the reaction.

$$\text{Conversion } /\% = (C_{glucose} - C_{glucose}') / C_{glucose} \times 100\ \%$$

Selectivity was based on the molar carbon concentration of the compounds according to the equations below, where $C_{glucose}$ indicates the molar carbon concentration of glucose before the reaction and $C_{glucose}$' indicates the molar carbon concentration of glucose after the reaction. $C_{fructose}$ indicates molar carbon concentration of fructose.

$$\text{Selectivity } /\% = C_{fructose} / (C_{glucose} - C_{glucose}') \times 100\ \%$$

Conversion of glucose into fructose

In a typical experiment, the catalyst (300 mg unless otherwise stated) and 300 mg glucose were placed in an intermittent high-pressure reactor (100 mL), and deionized water (30 mL) were added. The reactor was sealed and placed in a heating sleeve at the desired temperature. After the indicated reaction time, the reactor was cooled down with an ice-water bath and subsequently carefully opened.

Table S1 Glucose isomerization catalyzed by heterogeneous catalysts in water.

Catalysts	Temperature (°C)	Time (min)	Yield (%)	Selectivity (%)	Ref.
$MgO\text{-}ZrO_2$	95	360	35.7	70.0	[1]
$CaO\text{-}ZrO_2$	140	15	21.6	86.4	[2]
$Fe_3O_4@SiO_2$-TMG	120	60	25	54.3	[3]
ZrC	120	20	34	75.5	[4]
Hybrid tin-silicate	110	120	16.7	72.6	[5]
$Na_9Si_{12}Ti_5O_{38}(OH)$	100	120	39	84.8	[6]
$Na_3(Na,H)Ti_2O_2[Si_2O_6]^2$	100	120	34	63.6	[6]
$HKCa_2Si_8O_{19}$	100	120	34	64.2	[6]
$CaSi_6O_{17}$	100	120	35	68.6	[6]
DHT-4A2	90	9	9.6	96.0	[7]
Mg-Al-HT	110	30	30	88.2	[8]
Sn-Beta	110	30	31	57.4	[9]
Ti-Beta	140	90	23	46.0	[9]
Sn-MCM-41	140	90	12	92.3	[9]
MgNaY	100	30	31	86.1	[10]
Sn-MFI	80	120	27	73.0	[11]
MgO-NaY	100	100	33.8	67.6	[12]
Mg-Al-HT/C	90	120	40	76.0	[12]
$Mg\text{-}C_3N_4$	80	240	32.5	84.0	[13]
$Ca\text{-}C_3N_4$	90	240	28.4	87.9	[13]
$K\text{-}C_3N_4$	90	60	28.7	81.9	[13]
$Na\text{-}C_3N_4$	90	240	23.2	86.0	[13]
5Nb@UIO-66	120	420	43.1	61.7	[14]
CS/Ab	90	30	38.9	85.4	[15]
Al/HC180-300/O	180	5	42.6	83.6	[16]
Li/S-1	**50**	**60**	**40.7**	**99.9**	**Our work**

Table S2. ICP results of Li content in catalysts.

Catalysts	Li % (Theoretical loading)	Li % (After washing)	Li % (After reaction)
S-1	0	0	0
0.5 Li/S-1	0.5wt%	0.46wt%	0.47wt%
1 Li/S-1	1.0wt%	0.78wt%	0.77wt%
2 Li/S-1	2.0wt%	0.89wt%	0.93wt%

Table S3. BET analysis of Li/S-1 catalysts

Catalysts	BET surface/m^2•g	Pore width/nm
S-1	359.1501	3.03991
0.5 Li/S-1	301.8382	3.32120
1 Li/S-1	289.9329	3.28832
2 Li/S-1	292.6884	3.10826

Table S4. Py-IR analysis of S-1 zeolite and Li/S-1 catalyst

	Temperature (°C)	Weight (mg)	Brønsted acid concentration (umol/g)	Lewis acid concentration (umol/g)	Total*	B/L*
S-1 zeolite	200	17.2	2.401372	18.52171	20.92308	0.129652
	350	17.2	0.831244	0.767378	1.598622	1.083227
Li/S-1 catalyst	200	17.6	0.496438	22.97536	23.4718	0.021607
	350	17.6	0.180523	1.363523	1.544045	0.132394

Total*: Total acid content in catalyst, The Li loading is 1 wt% in all experiments.

B/L*: The mass ratios of Brønsted acid: Lewis acid

Table S5. The glucose conversion in different solvent.

	Solvent	Conversion %	Yield %	Selectivity %
1	H_2O	40.7	40.70	99.9
2	Methanol	8.6	8.6	99.9
3	Ethanol	7.3	7.3	99.9
4	Glycerol	~0	-	-
5	γ-Valerolactone	~0	-	-

Reaction condition: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mL H_2O and 50 °C. The Li loading is 1 wt% in all experiments.

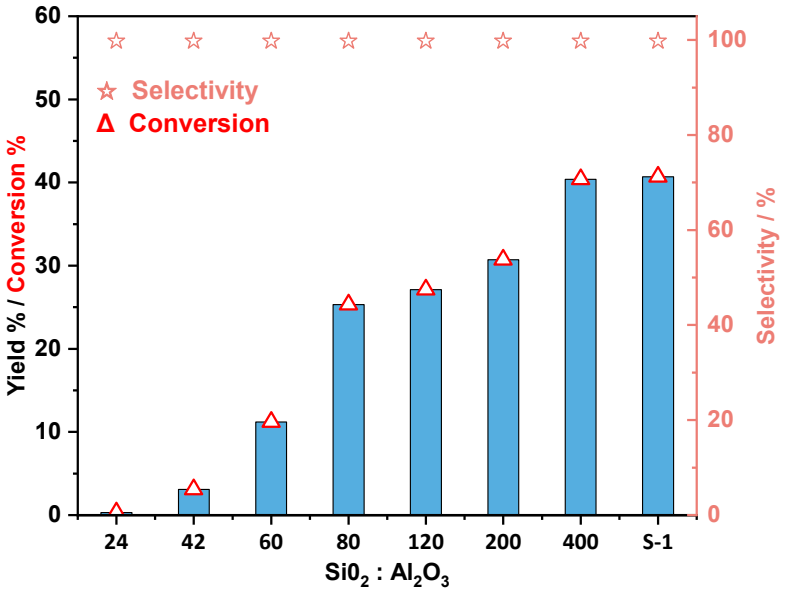

Figure S1. The results of glucose conversion over Li/ZSM-5 catalyst with different Si/Al ratios. Reaction conditions: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mL H_2O and 50 °C. The Li loading is 1 wt% in all experiments.

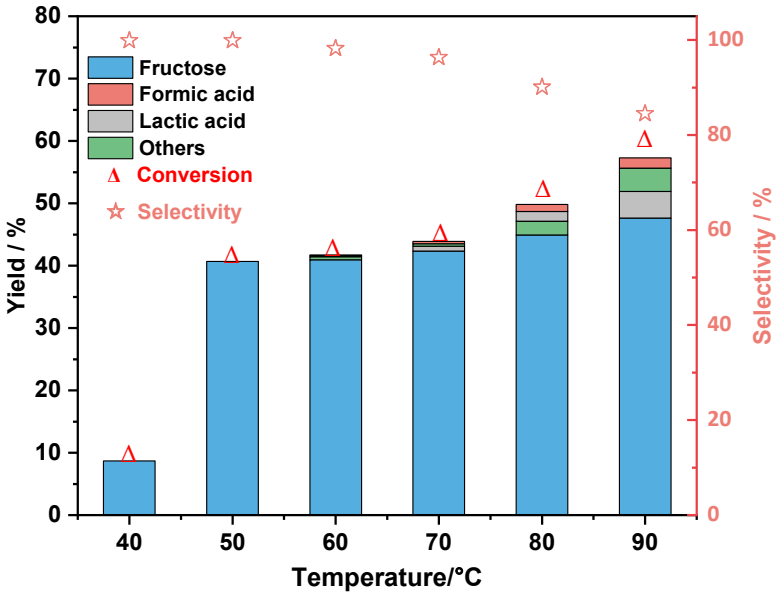

Figure S2. The results of glucose conversion over Li/S-1 catalyst at different temperature. Reaction conditions: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, and 30 mL H_2O. The Li loading is 1 wt% in all experiments.

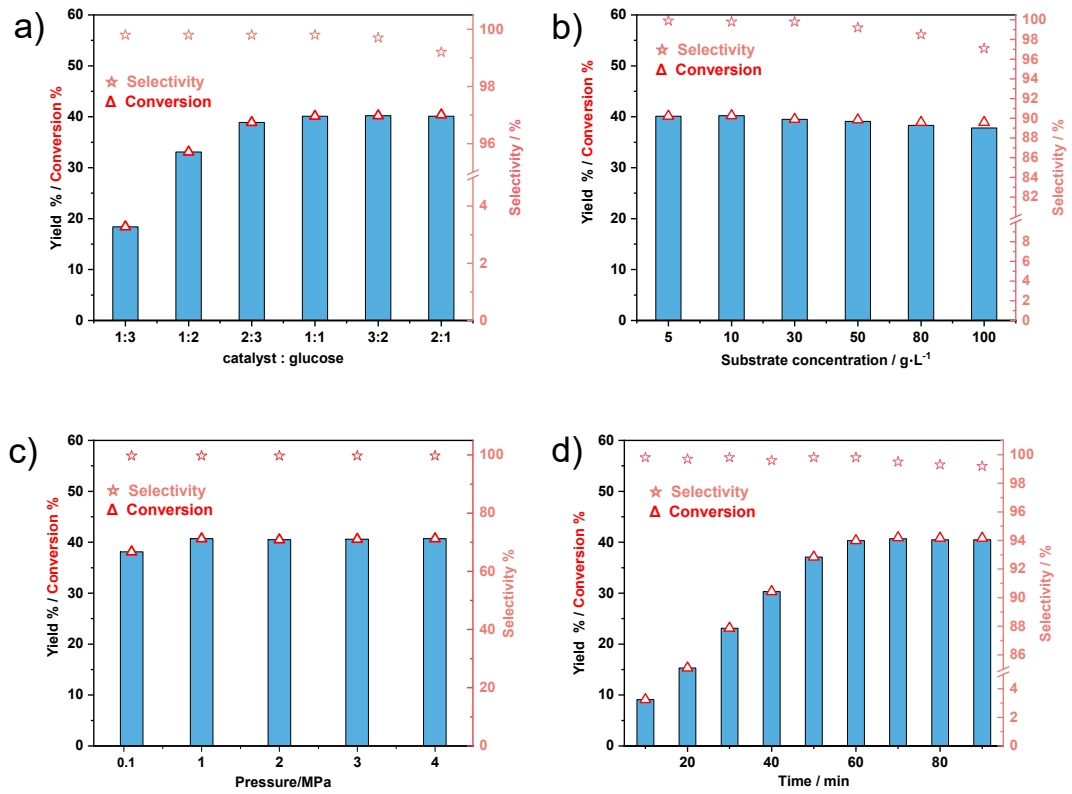

Figure S3. a) Different ratio of catalysts used in the conversion of glucose. **b)** Different concentration of glucose with the same ration of catalyst/glucose in the conversion of glucose over Li/S-1 catalyst. **c)** The influence of pressure in the conversion of glucose over Li/S-1 catalyst. **d)** The reaction of glucose in water over Li/S-1 catalyst with the prolong time. Reaction condition: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mL H_2O and 50 °C. The Li loading is 1 wt% in all experiments.

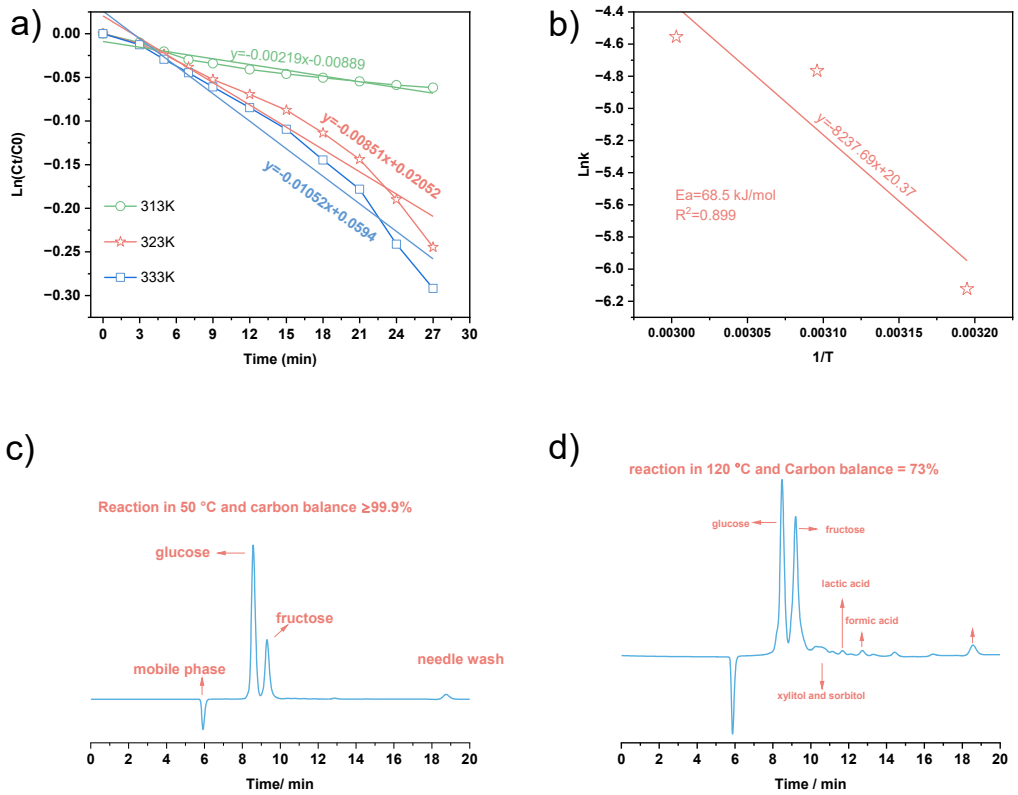

Figure S4. a) Reaction rate constants of glucose at different temperatures. **b,** Diagram of apparent activation energy of glucose over Li/S-1 catalyst. **c, d)** The HPLC results of glucose conversion over Li/S-1 catalyst in 50 and 100 °C. The Li loading is 1 wt% in all experiments.

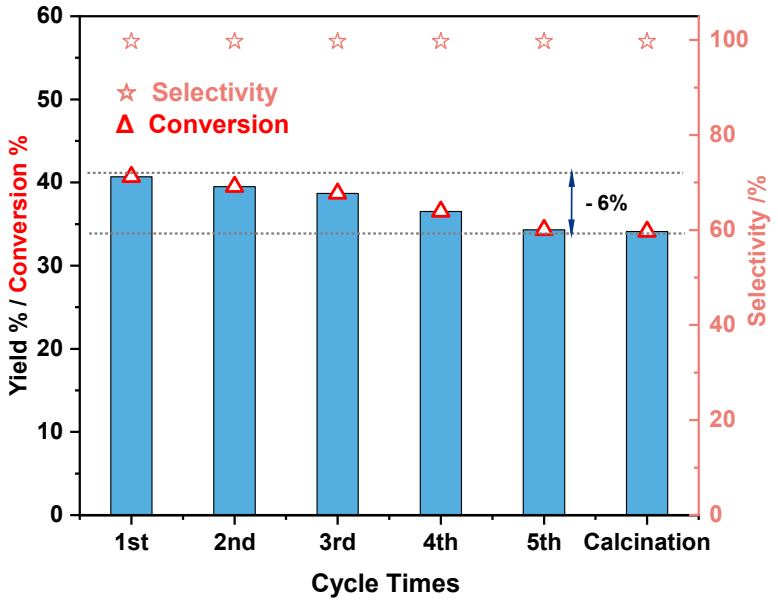

Figure S5. The results of glucose isomerization over Li/S-1 catalyst in 5 cycles. Reaction conditions: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mL H_2O and 50 °C. The Li loading is 1 wt% in all experiments.

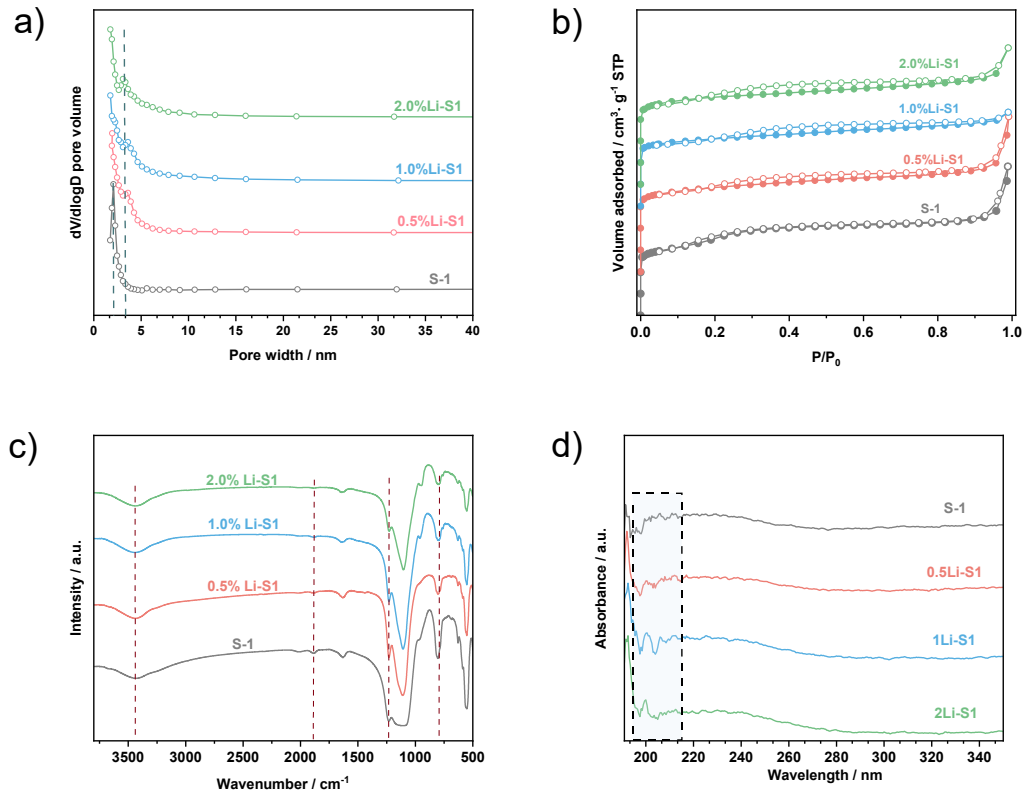

Figure S6. a) Pore size distribution and **b)** Hysteresis loop of Li/S-1 catalyst with different Li concentrations. c) FTIR spectra of Li/S-1 catalyst. d) UV-Vis of Li/S-1 catalyst

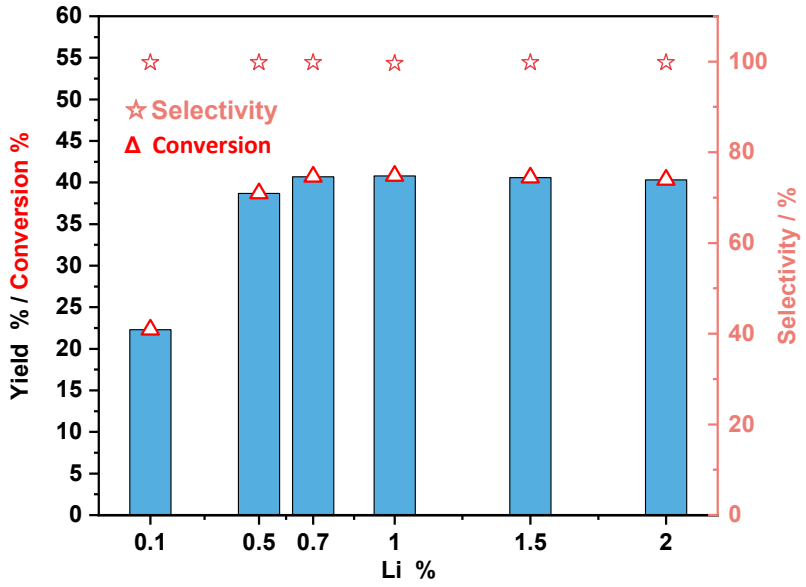

Figure S7. The results of glucose conversion over Li/S-1 catalyst with different Li concentrations. Reaction conditions: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mL H_2O and 50 °C.

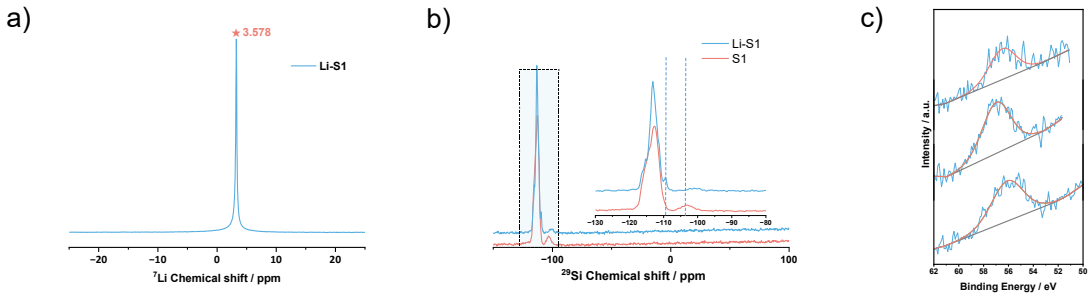

Figure S8. a) ^{7}Li solid state NMR spectrum of Li/S-1 catalyst. b) ^{29}Si solid state NMR spectrum of Li/S-1 catalyst. c) Li 1s XPS analysis of Li/S-1 catalyst with different Li concentrations.

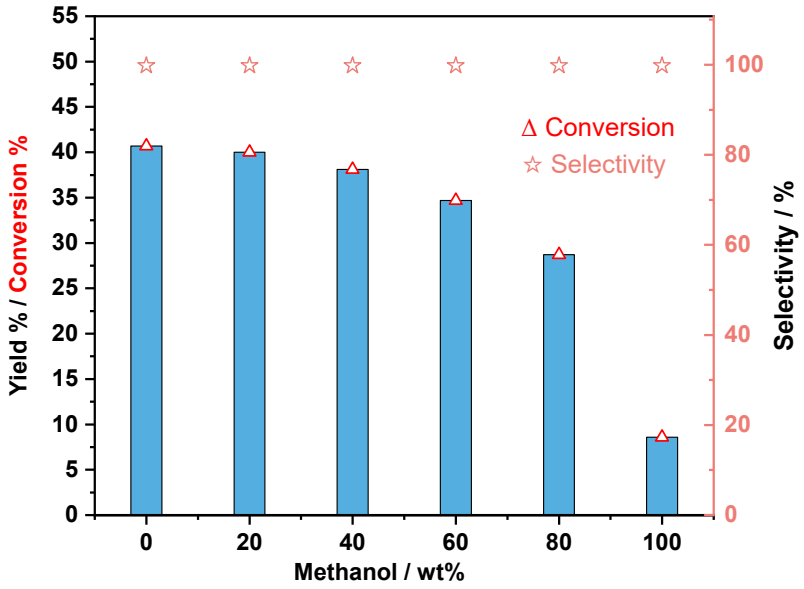

Figure S9. The results of glucose conversion over Li/S-1 catalyst with different ratio of methanol: water: Reaction conditions: 1 h, 1 MPa N_2, 300 mg glucose, 300 mg catalyst, 30 mg solution and 50 °C. The Li loading is 1 wt% in all experiments.

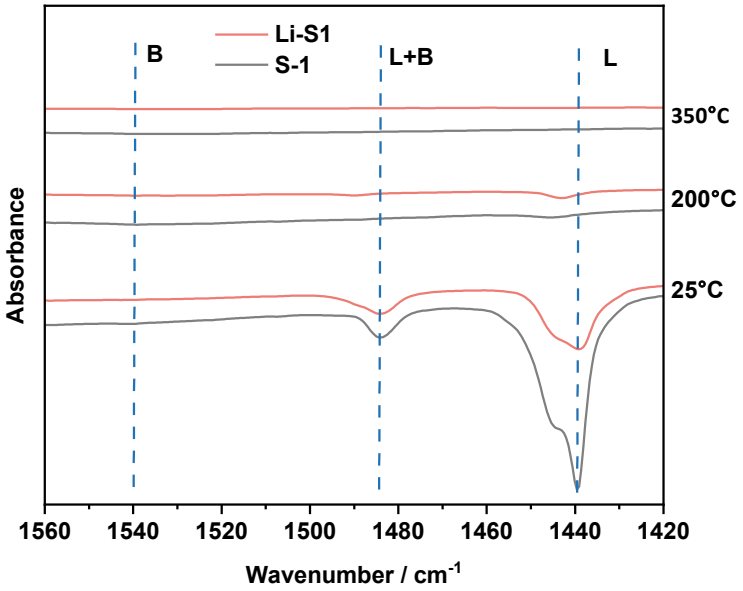

Figure S10. The Py-IR analysis of Li/S-1 catalyst.

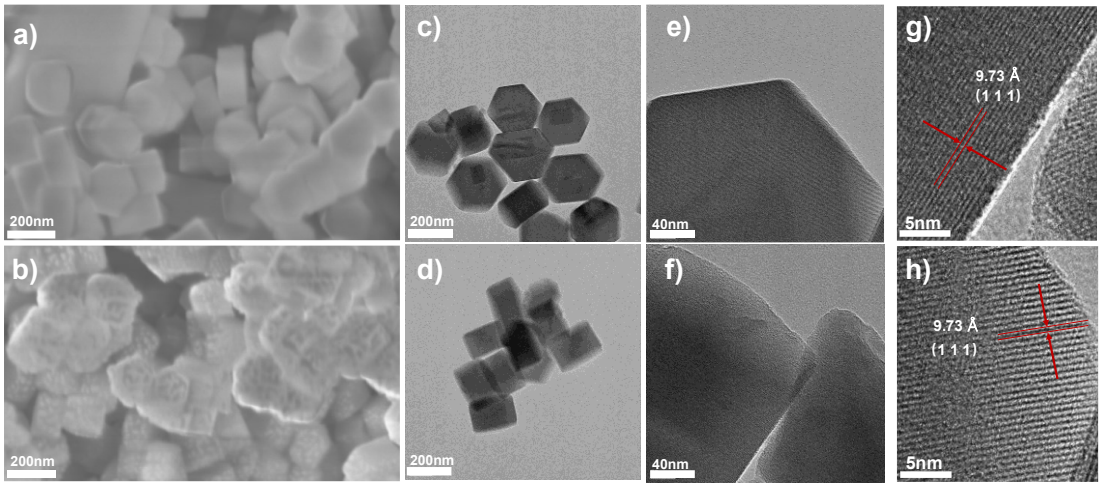

Figure S11. The SEM and TEM images of Li/S-1 catalyst and S-1 zeolite. S-1(**a, c, e, g**), Li-S1(**b, d, f, h**)

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