SUPPORTING INFORMATION

Efficient isomerization of glucose to fructose over zeolites in consecutive reactions in alcohol and aqueous media

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Catalytic Experiments

Chemicals: Glucose (99.5% purity), fructose (99% purity), and mannose (99% purity) were purchased from Sigma. Methanol (99.9% purity), ethanol (99.9% purity), 1-propanol (99.7% purity), and methanol-d_4 were obtained from Sigma–Aldrich. D-[2-^{13}C] fructose and D-[2,5-^{13}C] glucose were purchased from Omicron Biochemicals. All the commercially available zeolites used throughout the study were provided by Zeolyst International as pure compounds NH_4-form without content of binder materials. The received zeolites were calcined at 550 °C in air for 6 h prior to use in order to produce the acidic form.

Reaction procedure: Catalytic batch experiments were performed in an Ace pressure tube. In the first reaction step (step 1) 75 mg of zeolite catalyst, 125 mg of sugar and 4 g of alcohol or water were typically added and mixed in the pressure tube using a magnetic stirrer bar. The tube was then immersed into a preheated, thermally controlled oil bath and heated until the desired reaction temperature in the range 60-120 °C was reached. After a specific reaction time, the tube was removed from the oil bath and rapidly cooled down to room-temperature. In the reaction second step (step 2) 4 ml of water was added to the reaction mixture from step 1, where after the tube was re-immersed into the oil bath at 120 °C for 1 h and finally cooled down to room-temperature again.

Analysis procedure: Reaction samples were analyzed by high-pressure liquid chromatography (HPLC). Glucose was analyzed on a HPLC Agilent 1200 Series with a Aminex HPX-87H column (Bio-Rad) using 0.005 M aqueous sulfuric acid as eluent at a flow rate of 0.6 ml/min and a column temperature of 60 °C. Fructose, mannose and methyl fructoside were analyzed on a HPLC Agilent 1200 Series with a Rezex RCM-Monosaccharide Ca^{2+} column (Phenomenex) using MiliQ water as mobile phase at a flow rate of 0.6 ml/min and a column temperature of 80 °C. Both HPLC instruments were equipped with refractive index detectors. Fructose, mannose and their corresponding alkyl-derivatives merge at the same retention time using the Aminex column while the Monosaccharide column allowed separation. In contrast, glucose and methyl fructoside eluted at very similar retention times with the Monosaccharide column, so here the Aminex column was preferred. Glucose, fructose and mannose were quantified from standards, but it was not possible to purchase a standard of methyl fructoside

so here identification was made by ^{13}C NMR and the response factor obtained through several reactions from fructose at low temperature assuming no formation of others by-products. Catalytic results are shown as product distribution and reported in mol % (molar amount of each product present in the reaction mixture divided by the total molar amount of starting sugar).

Temperature Programmed Desorption (NH_3-TPD)

The number of acid sites present in the zeolites was measured by NH_3-TPD using an AutoChem II 2920 apparatus from Micromeritics. 100 mg of the sample was placed in a quartz reactor and degassed at 500 °C for 1 h in a flow of helium with a flow rate of 50 ml/min. The reactor was then cooled to 100 °C and ammonia (50 ml/min) was allowed to get adsorbed at the same temperature for 2 h. Before the ammonia desorption measurement, the sample was flushed with helium at a flow rate of 50 ml/min to remove any physisorbed ammonia. Ammonia desorption was measured every second from 100 to 500 °C at a ramp of 10 °C/min, and the number of acid sites calculated as the area under the desorption curve. The results are shown in Table S2. From the desorption data it can be deduced, that the zeolites contained both medium acid sites (desorption approx. between 100-270 °C) and strong acid sites (desorption approx. between 270-500 °C). The ratio of the number of medium acidic sites (type 1) to strong acidic sites (type 2) can be taken as a measure to define the relative efficiency of the catalysts in the formation of fructose from glucose.

^{13}C NMR Analyses

^{13}C NMR spectra were reported on a Bruker AM360 NMR spectrometer in CD_3OD and water at 25 °C, and peak positions are reported relative to the solvent (CD_3OD: δ/ppm = 48.27).

D-[2,5-^{13}C] glucose: ^{13}C NMR (75 MHz, CD_3OD) δ/ppm = 72.25, 73.15, 75.59, 77.32.

After reaction step 1 starting from glucose: ^{13}C NMR (75 MHz, CD_3OD) δ/ppm = 70.30, 71.10, 71.31, 72.24, 72.80, 72.83, 73.14, 74.35, 75.57, 77.22, 77.32, 78.56, 81.07, 82.75, 83.91, 100.78, 104.47, 108.47.

After reaction step 2 starting from glucose: ^{13}C NMR (75 MHz, CD_3OD) δ/ppm = 69.58, 69.73, 70.13, 70.2, 71.7, 71.93, 72.1, 73.52, 74.74, 81.33, 81.43, 83.53, 98.31, 100.55, 101.84, 103.55, 104.23, 108.45.

Table S1. One-pot synthesis of fructose from glucose in methanol-water mixtures. Reaction conditions: 75 mg H-USY (6), 125 mg glucose, 1 h, 120 °C.

MeOH in water (wt. %)	Product distribution (mol %)		
	Glucose	Fructose	Methyl fructoside
1	100	0	0
20	100	0	0
40	100	0	0
60	100	0	0
80	95	3	0
95	86	8	0
99	33	22	29

Table S2. Acidity measurements from NH_3-TPD.

Catalyst	Si/Al ratio	Acid sites type 1 (100-270 °C) (µmol/g)	Acid sites type 2 (270-500 °C) (µmol/g)	Total acid sites (µmol/g)	Acid sites type 1: type 2 ratio	Fructose (%)
H-Y	2.6	699	252	951	1:0.36	20
H-USY	6	461	374	835	1:0.81	55
	30	182	165	347	1:0.91	24
H-Beta	12.5	563	292	855	1:0.52	40
	19	440	366	806	1:0.83	29
	150	71	76	147	1:1.07	0

Table S3. Product distribution obtained for glucose conversion over commercial zeolite catalysts. Step 1: 75 mg catalyst, 125 mg glucose, 4 g methanol, 1 h, 120 °C.

Zeolite	Si/Al ratio	Products distribution (mol %)	
		Glucose	Fructose
Na-Y	2.6	88	12
Na-MOR	6.5	81	18
H-ZSM5	11.5	83	8
	25	77	11
	40	90	6
	140	95	4
H-MOR	10	93	4

Table S4. Chemical shift values of the tautomeric sugars obtained in isomerization experiments with ^{13}C labeled sugars in MeOH-d_4 and D_2O. Step 1: 20-22 mg ^{13}C-sugar, 10-11 mg H-USY (6), 3.5 g MeOH-d_4, 120 ^{o}C, 1 h; Step 2: 1 g D_2O, 120 ^{o}C, 1 h.

Tautomeric form	**Step**	**Chemical shift /ppm**				
		D-Glucose		**D-Mannose**		**D-Fructose**
		1-^{13}C	**2-^{13}C**	**1-^{13}C**	**2-^{13}C**	**2-^{13}C**
α-D-glucopyranose	1	92.8	72.7	-	-	-
	2	92.6	72.2	-	-	-
β-D-glucopyranose	1	97.0	75.1	-	-	-
	2	96.7	74.7	-	-	-
α-D-mannopyranose	1	-	-	94.7	72.1	-
	2	-	-	94.5	71.9	-
β-D-mannopyranose	1	-	-	94.5	71.8	-
	2	-	-	94.3	71.5	-
Methyl α-D-fructofuranoside	1	59.3	108.0	59.3	108.0	108.5
	2	58.9	108.1	58.9	108.1	108.5
Methyl β-D-fructofuranoside	1	60.3	104.0	60.2	104.0	104.5
	2	60.1	103.9	60.1	104.0	104.7
Methyl β-D-fructopyranoside	1	61.8	100.1	61.8	100.3	100.8
	2	61.4	100.4	61.4	100.5	100.8
α-D-fructofuranose	1	n.a.	n.a.	n.a.	n.a.	n.a.
	2	63.1	104.3	63.0	104.6	104.7
β-D-fructofuranose	1	n.a.	n.a.	n.a.	n.a.	n.a.
	2	63.6	101.7	63.5	101.9	101.9
β-D-fructopyranose	1	n.a.	n.a.	n.a.	n.a.	n.a.
	2	64.4	98.1	64.4	98.2	98.3
Major new peak 1	1	102.9	78.1	102.7	72.9	-
	2	103.1	77.4	102.7	72.5	-
Major new peak 2	1	109.8	80.6	109.1	77.2	-
	2	109.6	80.1	109.0	77.2	-

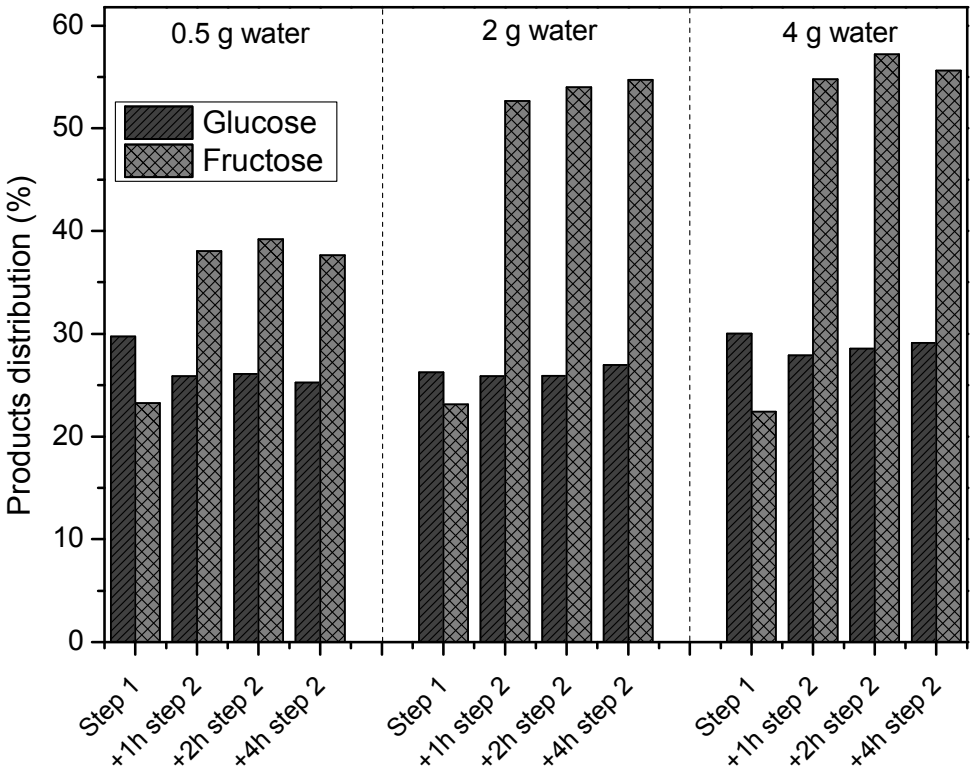


Figure S1. Optimization of the amount of water added and the reaction time for the hydrolysis step (Step 2). Step 1: 75 mg H-USY (6), 125 mg glucose, 4 g methanol, 1 h, 120 °C.

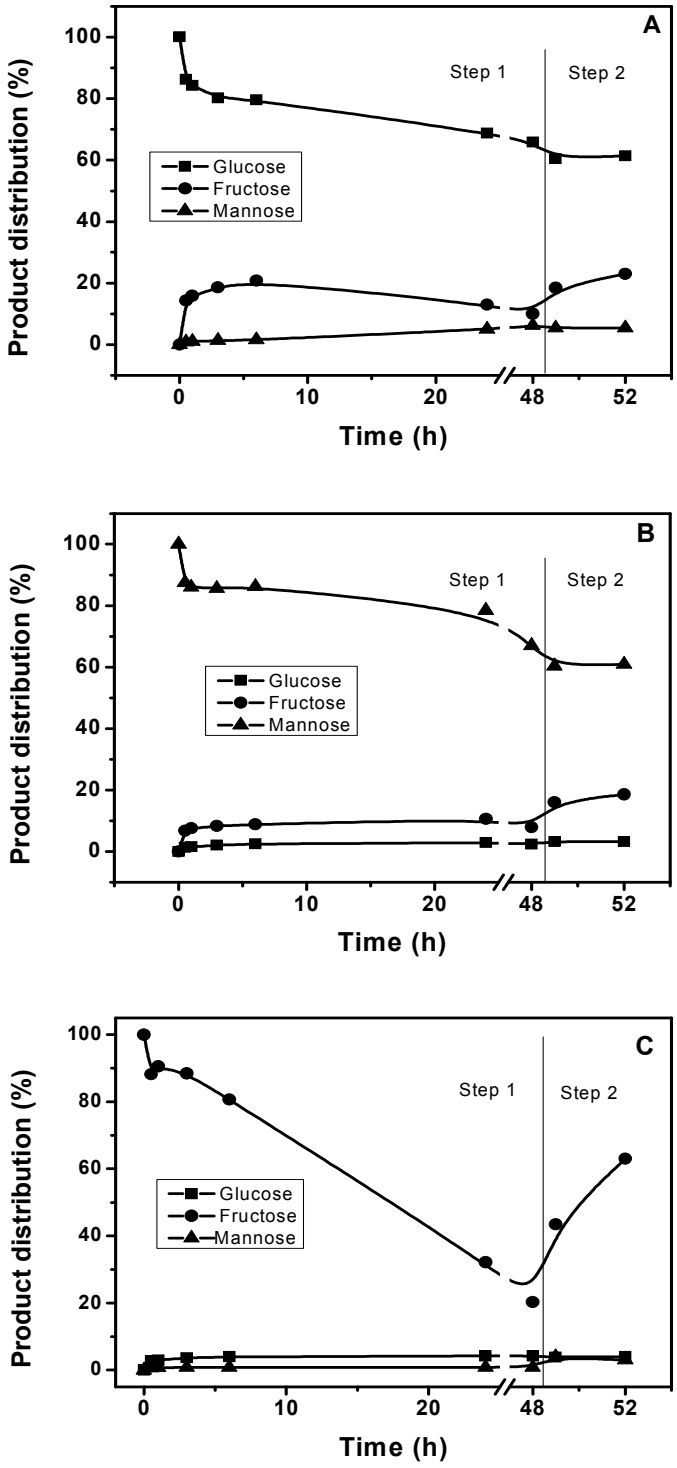


Figure S2. Influence of reaction time on the products distribution over Na-mordenite (6.5), starting from glucose (A), mannose (B) and fructose (C). Step 1: 75 mg Na-mordenite, 125 mg glucose, 4 g methanol, 120 °C; Step 2: 4 g water, 120 °C.

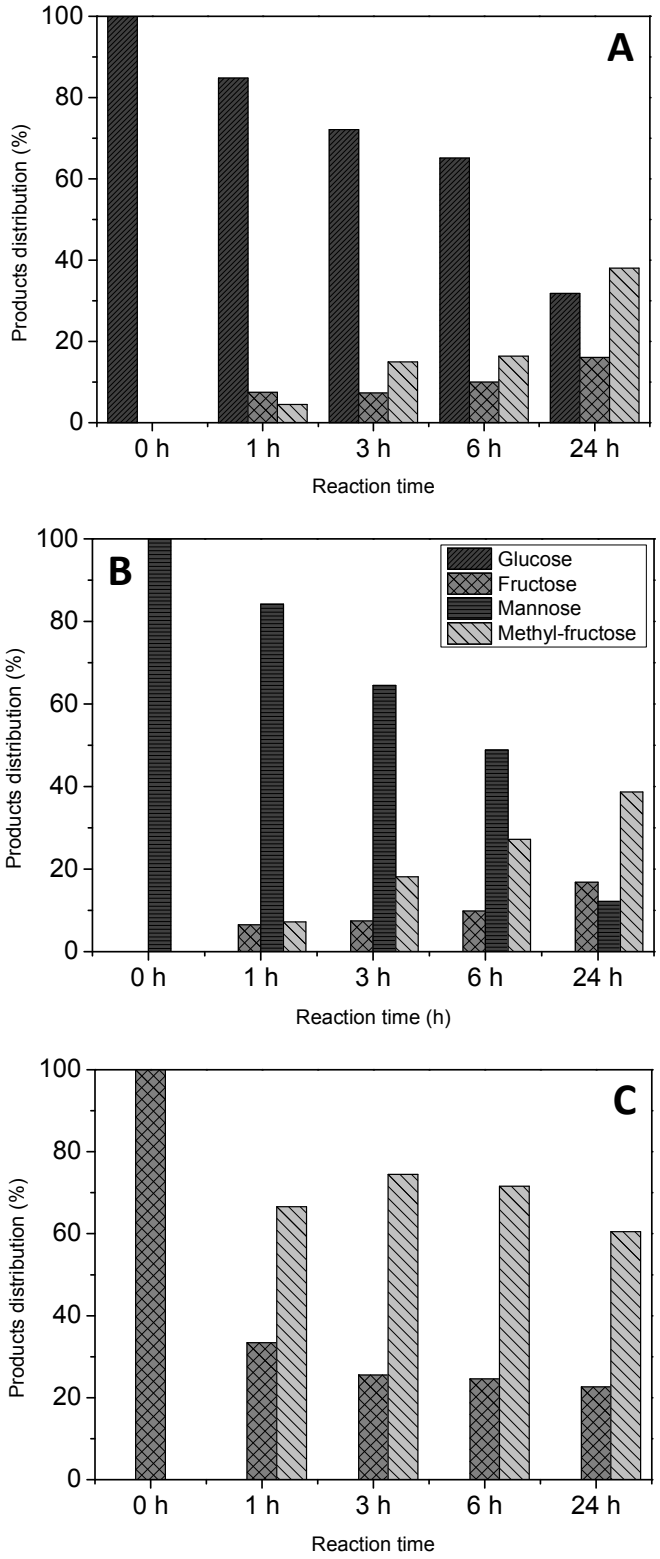
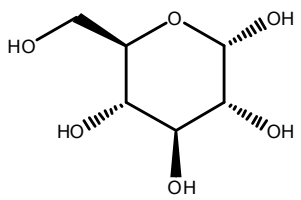
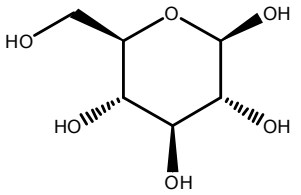


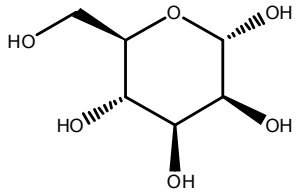
Figure S3. Influence of reaction time on the products distribution over H-USY (6), starting from glucose (A), mannose (B) and fructose (C). Step 1: 75 mg H-USY (6), 125 mg glucose, 4 g methanol, 80 °C.



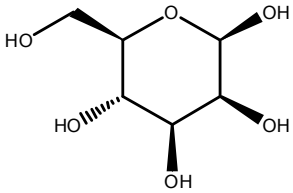
α-D-glucopyranoside



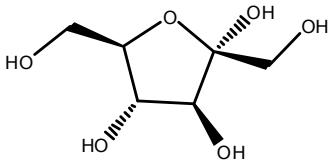
β-D-glucopyranoside



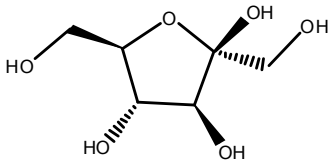
α-D-Mannopyranoside



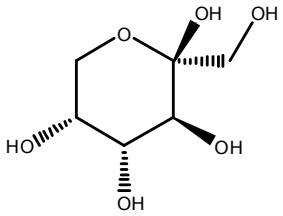
β-D-Mannopyranoside



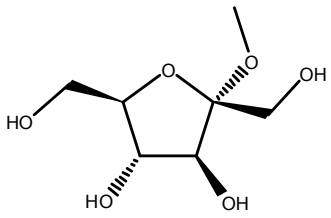
α-D-Fructofuranoside



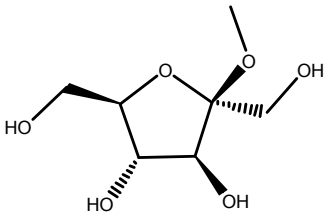
β-D-Fructofuranoside



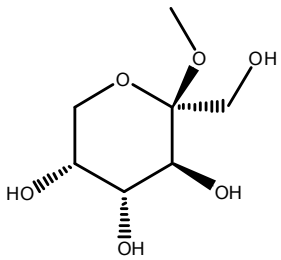
β-D-Fructopyranoside



Methyl α-D-Fructofuranoside



Methyl β-D-Fructofuranoside



Methyl β-D-Fructopyranoside

Scheme S1. Structures of selected sugar tautomers.