Confined synthesis of glucan oligomer from glucose in zeolites

Haotong Liang,[a] Sheng Ye,[a] Qiyu Liu,*[,b] Wei Fan[c] and Qiaozhi Ma*[,a]

[a] Key Laboratory for Biobased Materials and Energy of Ministry of Education, College of Engineering, South China Agricultural University, Guangzhou, 510640, China

[b] Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

[c] Department of Chemical Engineering, University of Massachusetts-Amherst, 159 Goessman Lab, 686 N Pleasant Street, Amherst, 01003, USA.

* Corresponding authors' emails:

liuqiyu@gdut.edu.cn (Qiyu Liu), maqzhi@scau.edu.cn (Qiaozhi Ma).

Table S1 Products distribution after glucose glycosylation

Catalyst	Temperature (℃)	Glucose Concentration (wt.%) [a]	Time (h)	Product Distribution (%)			Carbon Balance (%)
				Glucose [a]	Glucan Oligomer	Glucan	
H-Y	90	10	1	71.3	9.6	4.3	85.1
			2	37.5	12.3	33.4	83.3
			3	29.5	15.6	34.6	79.8
			4	21.6	26.9	31.4	79.8
			5	18.7	15.7	31.5	65.8
		15	1	58.4	18.5	23.3	100.3
			2	21.7	39.9	36.4	98.0
			3	18.1	37.2	41.7	97.0
			4	9.8	33.3	40.5	83.7
			5	8.3	31.7	50.1	90.1
		20	1	65.7	17.1	17.3	100.0
			2	32.7	33.3	30.4	96.4
			3	28.1	37.1	25.4	90.7
			4	25.2	32.7	29.2	87.1
			5	18.8	33.5	35.4	87.7
	100	10	1	41.5	17.3	37.3	96.1
			2	13.2	16.1	33.9	63.2
			3	7.7	22.8	39.1	69.6
			4	6.6	22.2	36.1	64.9
			5	5.3	21.4	38.9	65.5
		15	1	24.0	41.7	33.7	99.4
			2	8.2	40.6	46.3	95.1
			3	5.6	34.3	54.6	94.6

			4	0.9	33.1	52.3	86.3
			5	4.7	21.6	61.3	87.5
		20	1	27.1	43.4	27.1	97.7
			2	13.9	37.7	33.3	85.0
			3	10.3	30.7	41.6	82.6
			4	7.5	28.4	42.0	77.9
			5	9.2	25.1	43.4	77.6
H-MOR	90	10	1	26.5	20.7	0	47.2
			2	31.4	26.2	0	57.6
			3	34.4	37.3	0	71.7
			4	31.1	44.7	0	75.8
			5	34.8	47.2	0	82.1
		15	1	15.5	11.1	10.2	36.8
			2	21.8	28.2	4.1	54.1
			3	26.7	39.4	1.4	67.5
			4	26.1	41.8	5.0	72.9
			5	30.0	45.6	1.9	77.5
		20	1	6.6	12.7	6.0	25.3
			2	3.6	30.7	5.5	39.8
			3	6.7	40.1	8.2	55.0
			4	14.2	44.0	6.9	65.1
			5	23.1	52.0	2.4	77.5
	100	10	1	26.3	41.8	0	68.1
			2	12.5	51.6	0	64.1
			3	4.7	57.5	0	62.2
			4	2.7	58.6	1.1	62.4
			5	3.2	52.3	1.8	57.3
		15	1	40.3	35.3	8.0	59.7
			2	21.7	48.6	5.3	78.3
			3	13.0	54.8	5.8	87.0
			4	3.8	60.7	1.5	96.2
			5	2.1	61.7	0.6	97.9
		20	1	43.0	37.1	6.3	86.4
			2	23.3	50.0	5.7	79.0
			3	12.7	58.2	7.9	78.8
			4	9.0	60.9	6.8	76.7
			5	6.7	58.4	6.4	71.5

[a]: Glucose concentration refers to the initial glucose concentration in aqueous solvent before zeolite impregnation. [b]: Glucose refers to the unreacted glucose detected in zeolite after reaction.

Table S2 Products distribution after glucose glycosylation in H-MOR

Mass Ratio of 4A Zeolite to Substrate	Product Distribution (%)			Carbon Balance (%)
	Glucose [a]	Glucan Oligomer	Glucan	
0	72.8	10.7	0	83.2
0.5	58.4	20.4	0	78.8
1.0	32.5	39.4	1.4	73.3
1.5	29.2	35.7	2.0	66.9
2.0	27.9	37.2	4.5	69.6

[a]: Glucose refers to the unreacted glucose detected in zeolite after reaction.

Table S3 Catalyst recycle and product distribution [a]

Catalyst	Recycle Time	Product Distribution (%)			Carbon Balance (%)
		Glucose [a]	Glucan Oligomer	Glucan	
H-Y	1	24.0	41.7	33.7	99.4
	2	25.9	37.2	30.7	96.8
	3	26.9	38.9	31.2	97.0
	4	25.3	37.8	32.8	95.9
	5	21.6	40.2	31.0	92.8
H-MOR	1	3.8	61.7	0.6	66.0
	2	9.8	55.6	0.5	61.9
	3	9.8	54.3	0.8	64.9
	4	10.6	51.4	0.7	62.7
	5	15.9	46.3	0.6	62.8

[a]: Product distribution obtained from glucose glycosylation catalyzed by (a) H-Y and (b) H-MOR for different recycle times. Reaction condition: 100 ℃, 3 h with 15 wt.% of initial glucose dosage, ratio of 4A zeolite to substrate at 1:1. H-Y catalysis reaction condition: 1 h; H-MOR catalysis reaction condition: 5 h.