Supplementary Information for

Selective transformation of hemicellulose (xylan) into *n*-pentane, pentanols or xylitol over rhenium-modified iridium catalyst combined with acids

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Table S1 Elemental analysis of xylan

Entry	Xylan	C / wt%	H / wt%	S / wt%	N / wt%	K^+ / mg·g^{-1}	Na^+/ mg·g^{-1}
1	TCI	40.74	6.06	0.91	-	0.14	11.66
2	Wako	41.46	6.34	1.04	-	0.15	11.33
3	Sigma-Aldrich	41.08	6.24	0.90	-	0.17	13.59

Table S2 Products distribution in different phases for the results of Table 1, Entry 5

Organic Phase (GC column: DB-1)		Aqueous Phase (GC column: TC-WAX)		Gas Phase (GC column: Rtx-1-PONA)	
Products	Yield / %	Products	Yield / %	Products	Yield / %
n-Butane	1.79	1-Pentanol	0.00	*n*-Hexane	0.20
2-Methylbutane	1.33	2-Pentanol	0.00	2-Methylbutane	0.20
n-Pentane	63.02	3-Pentanol	0.00	*n*-Pentane	7.36
Cyclopentane	0.93	1-Hexanol	0.00	*n*-Butane	1.66
2-Methylpentane	0.00	2-Hexanol	0.00	Propane	0.35
3-Methylpentane	0.89	3-Hexanol	0.00	Ethane	0.88
n-Hexane	7.11			Methane	0.50
2-Methyltetrahydrofuran	0.58				
2 and 3-Pentanol	0.88				
Tetrahydropyran	0.00				
2,5-Dimethyltetrahydrofuran	0.00				
2-Methytetrahydropyran	0.22				
1-Pentanol	0.00				
3-Hexanol	0.00				
2-Hexanol	0.00				
1-Hexanol	0.00				

Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, HZSM-5: 0.06 g, H_2SO_4: 40 mg, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 24 h.

Table S3 Products distribution in different phases for the results of Table 5, Entry 2

Organic Phase (GC column: DB-1 and TC-WAX[1])		Aqueous Phase (GC column: TC-WAX)		Gas Phase (GC column: Rtx-1-PONA)	
Products	Yield / %	Products	Yield / %	Products	Yield / %
n-Butane	0.77	1-Pentanol	0.55	*n*-Hexane	0.01
2-Methylbutane	0.00	2-Pentanol	6.54	2-Methylbutane	0.00
n-Pentane	20.88	3-Pentanol	7.51	*n*-Pentane	0.61
Cyclopentane	0.21	1-Hexanol	0.00	*n*-Butane	0.15
2-Methylpentane	0.00	2-Hexanol	0.30	Propane	0.05
3-Methylpentane	0.36	3-Hexanol	0.28	Ethane	0.60
n-Hexane	1.34			Methane	0.25
2-Methyltetrahydrofuran	1.80				
3-Pentanol	9.77				
2-Pentanol	6.87				
Tetrahydropyran	0.18				
2,5-Dimethyltetrahydrofuran	0.00				
2-Methytetrahydropyran	0.00				
1-Pentanol	0.75				
3-Hexanol	1.02				
2-Hexanol	1.60				
1-Hexanol	0.00				

Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, H_2SO_4: 40 mg, *n*-dodecane: 20 ml, 413 K, initial H_2: 6 MPa, 144 h.

1: for separation of 2- and 3-pentanols

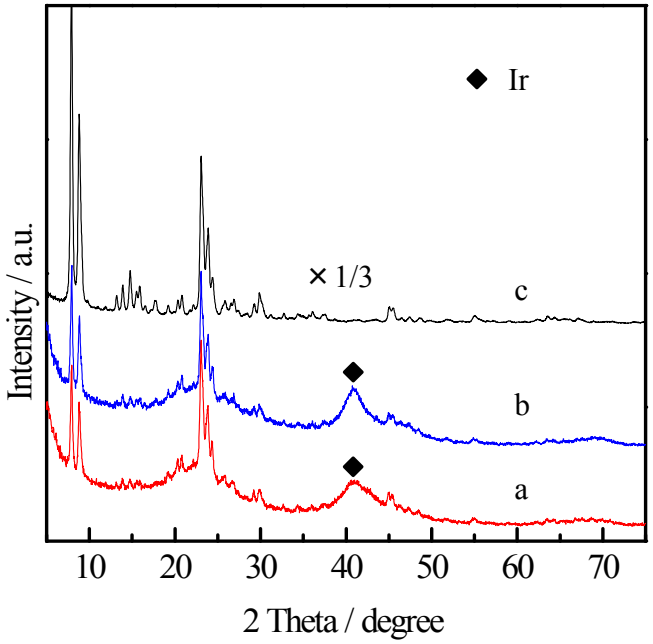

Fig. S1 XRD patterns of Ir-ReO_x/SiO_2 catalyst combined with HZSM-5. (a) after 1st reaction, (b) after 4th reaction, (c) HZSM-5.

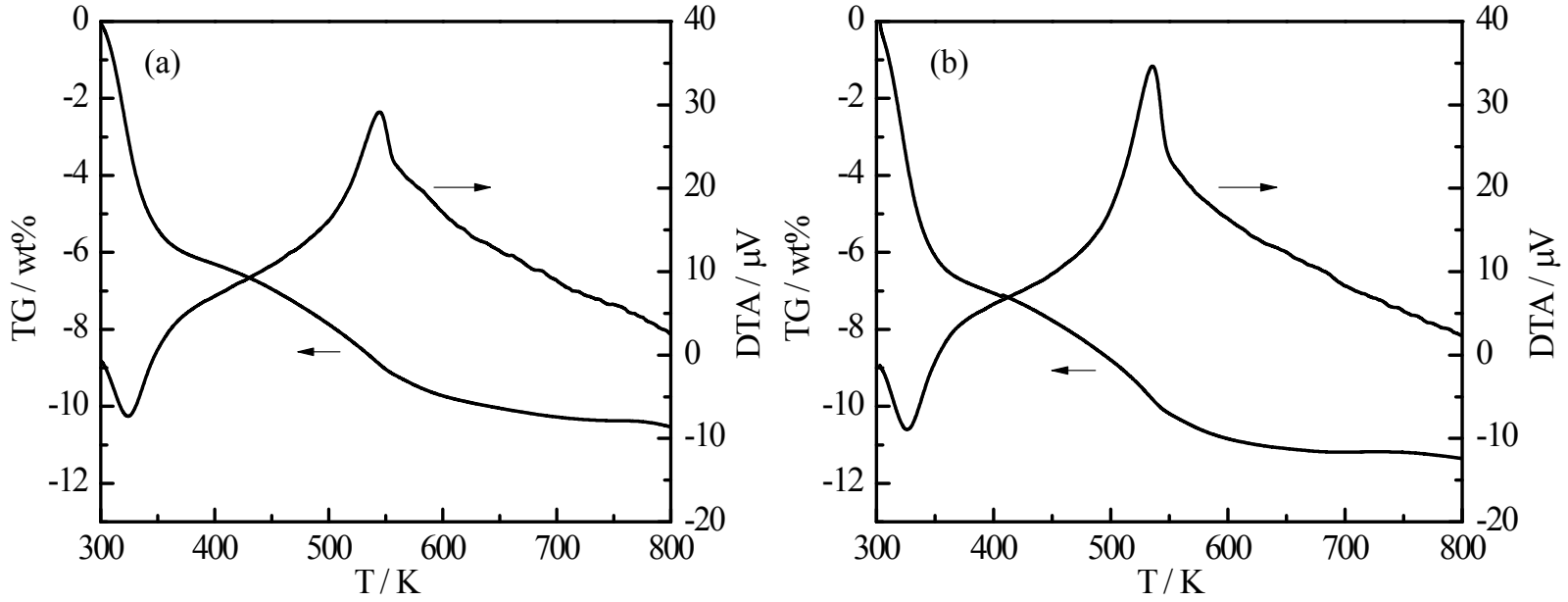

Fig. S2 TG-DTA profiles of Ir-ReO_x/SiO_2 + HZSM-5 after reaction. Measurement conditions: sample weight ~9 mg, heating rate 10 K/min, in air. Reaction conditions: Xylan: 0.5 g, H_2O: 9.5 g, *n*-dodecane: 4 ml, Ir-ReO_x/SiO_2 (Re/Ir=2): 0.15 g, HZSM-5 (Si/Al_2=90): 0.06 g, H_2SO_4: 40 mg, initial H_2: 6 MPa, 463 K, (a): 24 h, (b): 0.5 h.

Table S4 The effect of humins on Ir-ReO_x/SiO_2 + HZSM-5 catalysts for conversion of xylitol to *n*-pentane

Entry	Ir-ReO_x/SiO_2 catalyst	pH	Conversion / %	Yield / %						Loss of carbon balance
				n-Pentane	Other pentanes	Cyclic ethers	1-PeOH	2- and 3-PeOH	C1-C4 alkanes	
1	Fresh	1.88	>99	63	0.5	7.4	4.2	1.0	2.5	21
2	After xylan reaction 0.5h, then calcined at 773 K for 3 h	1.84	>99	52	0.4	7.0	3.5	0.8	1.9	34
3	After xylan reaction 0.5h, without calcination	1.86	>99	11	0.1	3.5	3.8	0.0	0.4	81

Other hexanes: 2-methylpentane and 3-methylpentane, Other pentanes: 2-methylbutane and cyclopentane, HxOH: Hexanol; PeOH: Pentanol; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C1-C4 alkanes: methane, ethane, propane and *n*-butane.
Xylan reaction conditions were the same as shown in Fig. S2b.
Reaction conditions: xylitol: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, HZSM-5: 0.06 g, H_2SO_4: 10 mg, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 0.5 h.

Table S5 Conversion of pentanols catalyzed by H_2SO_4

Entry	Substrate	Conversion / %	Yield / %		
			1-pentene	2-pentene	Others
1	1-pentanol	<0.01	<0.01	<0.01	<0.01
2	2-pentanol	2.5	0.2	2.2	0.1
3	3-pentanol	4.9	0.1	4.5	0.3

Others: unidentified products
Reaction conditions: Substrate: 0.5 g, H_2SO_4: 60 mg, H_2O: 9.5 g, *n*-dodecane: 20 ml, initial H_2: 6 MPa, 413 K, 2 h.

Table S6 Conversion of xylan to pentanols over Ir-ReO_x/SiO_2 + H_2SO_4

Entry	Time / h	Conversion / %	Yield / %										Loss of carbon balance
			Sum of PeOHs	1-PeOH	2-PeOH	3-PeOH	HxOHs	Pentanes	Hexanes	C1-C4 alkanes	Cyclic ethers	Xylitol	
1	24	94	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.4	0.3	71	22
2	48	95	1.3	1.0	0.0	0.4	0.4	0.4	0.0	0.5	0.4	59	33
3	96	94	16	6.0	2.4	7.8	2.2	5.8	0.5	1.0	1.3	0.0	67
4	120	95	21	6.0	4.4	10	2.5	8.9	0.8	1.1	1.5	0.0	59
5	144	95	32	1.3	13	17	3.7	22	1.7	1.8	2.0	0.0	33
6	168	98	29	0.5	12	16	4.3	31	2.3	1.8	2.3	0.0	0.0

PeOH: Pentanol; HxOH: Hexanol; Pentanes: *n*-pentane, 2-methylbutane and cyclopentane, Hexanes: *n*-hexane, 2-methylpentane and 3-methylpentane, C1-C4 alkanes: methane, ethane, propane and *n*-butane; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran.
Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, H_2SO_4: 40 mg, *n*-dodecane: 20 ml, 413 K, initial H_2: 6 MPa.

Table S7 Conversion of xylan to xylitol over different catalysts

Entry	Catalyst	Conversion / %	Yield / %						Loss of carbon balance	pH
			Xylitol	Arabitol	Xylose	Arabinose	Sorbitol	Alkanes		
1	Ir-ReO_x/SiO_2	97	79	0.8	0.0	0.0	2.3	0.1	15	2.17
2	Pd/C	94	61	1.7	13	0.6	0.1	0.2	17	2.16
3	Ru/C	92	37	28	0.0	0.0	3.5	0.8	23	2.16
4	Pt/C	90	11	0.9	66	0.3	0.3	0.3	11	2.15
5	Rh/C	85	10	0.7	70	0.4	0.0	0.3	3.9	2.16

Alkanes: C1-C6 alkanes

Reaction conditions: TCI Xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, H_2SO_4: 30 mg, initial H_2: 6 MPa, 403 K, 12 h.